

JC19 Rec'd PCT/PTO 24 MAY 2001

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TRANSMITTAL LETTER TO THE UNITED STATES

ATTORNEY'S DOCKET NUMBER 0732/990001

DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

09/856695

INTERNATIONAL APPLICATION NO. PCT/EP 99/08849	INTERNATIONAL FILING DATE 18 November 1999	PRIORITY DATE CLAIMED 11 January 1999 25 November 1998
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TITLE OF INVENTION: PURIFICATION OF METALLOCENES

APPLICANT(S) FOR DO/EO/US Carsten BINGEL, Patrik MUELLER, Hans - Herbert BRINTZINGER,
Hans-Robert-Hellmuth DAMRAUApplicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following
items and other information:

1. /X/ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. / / This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. /X/ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. /x / A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. /X/ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. /X/ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. / / has been transmitted by the International Bureau.
 - c. / / is not required, as the application was filed in the United States Receiving Office (RO/USO).
6. /X/ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. / / Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - a. / / are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. / / have been transmitted by the International Bureau.
 - c. / / have not been made; however, the time limit for making such amendments has NOT expired.
 - d. / / have not been made and will not be made.
8. / / A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. /X / An oath or declaration of the inventor(s) (35 U.S.C. 171(c)(4)).
10. / / A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. /x / An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. /x / An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. /X / A FIRST preliminary amendment.
/ / A SECOND or SUBSEQUENT preliminary amendment.
14. / / A substitute specification.
15. / / A change of power of attorney and/or address letter.
16. /x / Other items or information.
International Search Report
International Preliminary Examination Report

09/856695

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U.S. Appl. No. (If Known) INTERNATIONAL APPLN. NO.
PCT/EP99/08849ATTORNEY'S DOCKET NO.
0732/99001

		CALCULATIONS	PTO USE ONLY
17. /X/ The following fees are submitted			
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):			
Search Report has been prepared by the EPO or JPO.....	\$860.00	860.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482).....\$750.00			
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)).....\$700.00			
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO\$ 970.00			
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4).....\$96.00			
ENTER APPROPRIATE BASIC FEE AMOUNT = \$		860.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than / / 20 / / 30 months from the earliest claimed priority date (37 CFR 1.492(e)).			
Claims	Number Filed	Number Extra	Rate
Total Claims	7 -20		X\$18.
Indep. Claims	1 -3		X\$80.
Multiple dependent claim(s) (if applicable)		+270.	
TOTAL OF ABOVE CALCULATION		=	860.00
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).			
SUBTOTAL		=	860.00
Processing fee of \$130. for furnishing the English translation later than / / 20 / / 30 months from the earliest claimed priority date (37 CFR 1.492(f)).			
TOTAL NATIONAL FEE		=	860.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) \$40.00 per property			
TOTAL FEES ENCLOSED		= \$	900.00
Amount to be refunded:		\$	
Charged		\$	

a./X/ A check in the amount of \$ 900. to cover the above fees is enclosed.

b./ / Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c./X/ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 11-0345. A duplicate copy of this sheet is enclosed.**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b) must be filed and granted to restore the application to pending status.**SEND ALL CORRESPONDENCE TO:**KEIL & WEINKAUF
1101 Connecticut Ave., N.W.
Washington, D. C. 20036

SIGNATURE

Herbert B. Keil

NAME

Registration No. 18,967

09/856695

JC18 Rec'd PCT/PTO 2 4 MAY 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of)
BINGEL et al.) BOX PCT
)
International Application)
PCT/EP 99/08849)
)
Filed: November 18, 1999)
)
For: PURIFICATION OF METALLOCENES

PRELIMINARY AMENDMENT

Honorable Commissioner of
Patents and Trademarks
Washington, D.C. 20231

Sir:

Prior to examination, kindly amend the above-identified application as follows:

IN THE CLAIMS

Please amend the claims as shown in the attached sheet.


REMARKS

The claims have been amended further to eliminate multiple dependency and to put them in better form for U.S. filing. No new matter is included. A clean copy of the claims is attached.

Favorable action is solicited.

Respectfully submitted,

KEIL & WEINKAUF


Herbert B. Keil
Reg. No. 18,967

1101 Connecticut Ave., N.W.
Washington, D.C. 20036

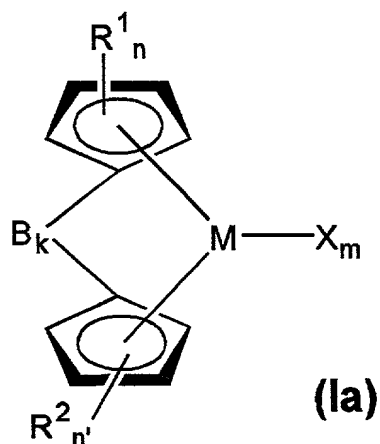
(202)659-0100

[illegible]

3. A process as claimed in claim 1 [or 2], wherein toluene, hexane, heptane, xylene, tetrahydrofuran (THF), dimethoxyethane (DME), toluene/THF, heptane/DME or toluene/DME is used in step d).

CURRENT CLAIMS - OZ 0732/990001

1. A process for purifying compounds of the formula (Ia)



where

M is a metal of transition group III, IV, V or VI of the Periodic Table of the Elements, in particular Ti, Zr or Hf, particularly preferably zirconium,

R¹ are identical or different and are each a radical SiR₃, where R¹² are identical or different and are each a hydrogen atom or a C₁-C₄₀ group, preferably C₁-C₂₀-alkyl, C₁-C₁₀-fluoroalkyl, C₁-C₁₀-alkoxy, C₆-C₂₀-aryl, C₆-C₁₀-fluoroaryl, C₆-C₁₀-aryloxy, C₂-C₁₀-alkenyl, C₇-C₄₀-arylalkyl, C₇-C₄₀-alkylaryl or C₈-C₄₀-arylalkenyl, or R¹ is a C₁-C₃₀ group, preferably C₁-C₂₅-alkyl such as methyl, ethyl, tert-butyl, cyclohexyl or octyl, C₂-C₂₅-alkenyl, C₃-C₁₅-alkylalkenyl, C₆-C₂₄-aryl, C₅-C₂₄-heteroaryl, C₇-C₃₀-arylalkyl, C₇-C₃₀-alkylaryl, fluorinated C₁-C₂₅-alkyl,

fluorinated C₆-C₂₄-aryl, fluorinated C₇-C₃₀-arylalkyl, fluorinated C₇-C₃₀-alkylaryl or C₁-C₁₂-alkoxy,

or two or more radicals R¹ may be joined to one another in such a way that the radicals R¹ and the atoms of the cyclopentadienyl ring which connect them form a C₄-C₂₄-ring system which may in turn be substituted,

R² are identical or different and are each a radical SiR₃¹², where R¹² are identical or different and are each a hydrogen atom or a C₁-C₄₀ group, preferably C₁-C₂₀-alkyl, C₁-C₁₀-fluoroalkyl, C₁-C₁₀-alkoxy, C₆-C₁₄-aryl, C₆-C₁₀-fluoroaryl, C₆-C₁₀-aryloxy, C₂-C₁₀-alkenyl, C₇-C₄₀-arylalkyl, C₇-C₄₀-alkylaryl or C₈-C₄₀-arylalkenyl, or R² is a C₁-C₃₀ group, preferably C₁-C₂₅-alkyl such as methyl, ethyl, tert-butyl, cyclohexyl or octyl, C₂-C₂₅-alkenyl, C₃-C₁₅-alkylalkenyl, C₆-C₂₄-aryl, C₅-C₂₄-heteroaryl, C₇-C₃₀-arylalkyl, C₇-C₃₀-alkylaryl, fluorinated C₁-C₂₅-alkyl, fluorinated C₆-C₂₄-aryl, fluorinated C₇-C₃₀-arylalkyl, fluorinated C₇-C₃₀-alkylaryl or C₁-C₁₂-alkoxy, or two or more radicals R² may be joined to one another in such a way that the radicals R² and the atoms of the cyclopentadienyl ring which connect them form a C₄-C₂₄ ring system which may in turn be substituted,

X is a halogen atom, in particular chlorine,

n is from 1 to 5 when k = 0, and n is from 0 to 4 when k = 1,

n' is from 1 to 5 when k = 0, and n' is from 0 to 4 when k = 1,

m is from 1 to 4, preferably 2,

k is zero or 1, where the metallocene is unbridged when $k = 0$ and is bridged when $k = 1$, with preference being given to $k = 1$, and

B is a bridging structural element between the two cyclopentadienyl rings,

comprising the steps:

a) reacting the compound of the formula (Ia) with a ligand exchange component



where

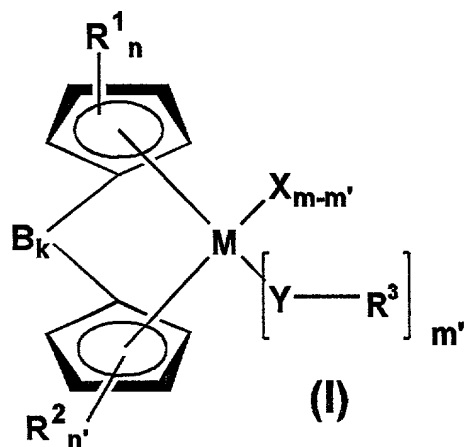
M^1 is a cation or a cationic fragment, in particular Li, Na, K, MgCl, MgBr, MgI, or is an ammonium cation corresponding to an amine,

R^3 is hydrogen or a C_1 - C_{40} group, preferably C_1 - C_{25} -alkyl such as methyl, ethyl, tert-butyl, cyclohexyl or octyl, C_2 - C_{25} -alkenyl, C_3 - C_{15} -alkylalkenyl, C_6 - C_{24} -aryl, C_5 - C_{24} -heteroaryl such as pyridyl, furyl or quinolyl, C_7 - C_{30} -arylalkyl, C_7 - C_{30} -alkylaryl, fluorinated C_1 - C_{25} -alkyl, fluorinated C_6 - C_{24} -aryl, fluorinated C_7 - C_{30} -arylalkyl or fluorinated C_7 - C_{30} -alkylaryl,

Y is an element of main group 6 of the Periodic Table of the Elements, in particular oxygen or sulfur, or a fragment CR^3_2 , NR^3 , $NR^3(CO)-$, $NR^3(SO_2)-$,

PR^3 or $P(=O)R^3$, $O(CO)-$, $O(SO_2)-$,

to form the compound of the formula (I)



where

M , R^1 , R^2 , R^3 , X , Y , n , n' , m , k , B and R^{12} are as defined above and

m' is from 1 to 4, preferably 1 or 2,

with the compound of the formula M^1X , where M^1 and X are as defined above, being eliminated, in an inert solvent or solvent mixture,

- b) if desired, separating off solid residues of the formula M^1X
 - c) if desired, separating off the inert solvent or solvent mixture,
 - d) recrystallizing the compound of the formula (I) from an aprotic hydrocarbon,
 - e) separating the compound of the formula (I) from the mother liquor.
2. A process as claimed in claim 1, wherein a polar or nonpolar, aprotic hydrocarbon

or hydrocarbon mixture is used in step d).

3. A process as claimed in claim 1, wherein toluene, hexane, heptane, xylene, tetrahydrofuran (THF), dimethoxyethane (DME), toluene/THF, heptane/DME or toluene/DME is used in step d).
4. The use of a compound obtained as set forth in claim 1 for preparing a catalyst system for the polymerization of olefins.
5. A catalyst system comprising at least one compound obtained as set forth in claim 1 and a support and, if desired, a cocatalyst.
6. A process for preparing a polyolefin in the presence of a catalyst system as claimed in claim 5.
7. The use of a catalyst as claimed in claim 5 for the polymerization of one or more olefins.

Purification of metallocenes

The present invention relates to a process for purifying
5 metallocenes, in which a sparingly soluble metallocene halide is
converted into a readily soluble and readily crystallizable
metallocene by replacement of at least one halide ligand by an
alternative negatively charged ligand and the metallocene
obtained in this way is subsequently purified by crystallization.

10

Metallocenes can, if appropriate in combination with one or more
cocatalysts, be used as catalyst components for the
polymerization and copolymerization of olefins. In particular,
halogen-containing metallocenes are used as catalyst precursors
15 which can be converted into a polymerization-active cationic
metallocene complex by means of, for example, an aluminoxane
(EP-A-129368).

The preparation of metallocenes is known per se (US 4,752,597; US
20 5,017,714; EP-A-320762; EP-A-416815; EP-A-537686; EP-A- 669340;
H.H. Brintzinger et al.; Angew. Chem., 107 (1995), 1255; H.H.
Brintzinger et al., J. Organomet. Chem. 232 (1982), 233). For
example, cyclopentadienyl-metal compounds can be reacted with
halides of transition metals such as titanium, zirconium and
25 hafnium. The metallocene dihalides formed, generally the
metallocene dichlorides, are, in the case of the industrially
interesting racemic ansa-bisindenyl-metallocenes which are
required for the preparation of isotactic polypropylene (EP
0485823, EP 0549900, EP 0576970, WO 98/40331), generally
30 sparingly soluble compounds. The crude products formed in the
syntheses comprise not only the desired metallocenes but also
considerable amounts of inorganic by-products (e.g. salts),
organometallic by-products (e.g. isomers) and organic by-products
(e.g. unreacted substituted cyclopentadienyl ligands). When
35 metallocenes are used as catalyst components, both in homogeneous
and in heterogeneous catalyst systems, the by-products adversely
affect the catalyst activity in olefin polymerization.

For purifying the crude products comprising desired racemic
40 ansa-bisindenyl-metallocene, methods by means of which inorganic,
organometallic and organic by-products can be separated from the
desired metallocene are known. In US 5,455,366 and EP 576970, the
racemic metallocenes are freed of lithium chloride, the meso
isomer and organic impurities by extraction with methylene
45 chloride and subsequent crystallization. In DE 19547247 and DE
19547248, the crude products from the metallocene synthesis are
freed of the undesirable by-products by treatment with polar

and/or protic solvents. In US 5,556,997, a metallocene contaminated with tetrahydrofuran-containing by-products is purified further by treatment with tetrahydrofuran.

- 5 Although the major part of the by-products can be separated from the desired racemic metallocene using the known methods, the catalysts prepared using the metallocenes which have been purified in this way, in particular supported catalysts, frequently display unsatisfactory activity, or the proportion of
- 10 undesirable low molecular weight polyolefins, known as extractables, is too high. If metallocenes purified by a further recrystallization are used as catalyst components, the abovementioned disadvantages in the polymerization can be avoided. However, large amounts of solvent are required because
- 15 of the sparing solubility of the industrially relevant ansa-bisindenyl-metallocene dichlorides. Simple recrystallization of the metallocene dichlorides is thus an uneconomical process step.
- 20 It is an object of the present invention to find an economical purification process by means of which metallocenes of the required quality can be obtained.

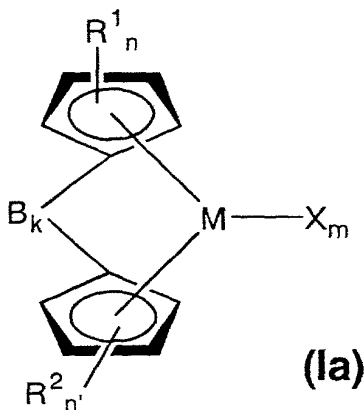
- We have found that this object is achieved by a simple process in
- 25 which the sparingly soluble, insufficiently pure metallocene dihalides are converted into more soluble and readily crystallizable metallocenes by replacement of at least one halide ligand and the new metallocenes prepared in this way are obtained in purified form by removing insoluble constituents by
- 30 crystallization.

The present invention accordingly provides a process for purifying compounds of the formula (Ia)

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40

45



where

M is a metal of transition group III, IV, V or VI of the Periodic Table of the Elements, in particular Ti, Zr or Hf, particularly preferably zirconium,

R^1 are identical or different and are each a radical $Si(R^{12})_3$, where R^{12} are identical or different and are each a hydrogen atom or a C_1 - C_{40} group, preferably C_1 - C_{20} -alkyl, C_1 - C_{10} -fluoroalkyl, C_1 - C_{10} -alkoxy, C_6 - C_{20} -aryl, C_6 - C_{10} -fluoroaryl, C_6 - C_{10} -aryloxy, C_2 - C_{10} -alkenyl, C_7 - C_{40} -arylalkyl, C_7 - C_{40} -alkylaryl or C_8 - C_{40} -arylalkenyl,

or R^1 is a C_1 - C_{30} group, preferably C_1 - C_{25} -alkyl such as methyl, ethyl, tert-butyl, cyclohexyl or octyl, C_2 - C_{25} -alkenyl, C_3 - C_{15} -alkylalkenyl, C_6 - C_{24} -aryl, C_5 - C_{24} -heteroaryl, C_7 - C_{30} -arylalkyl, C_7 - C_{30} -alkylaryl, fluorinated C_1 - C_{25} -alkyl, fluorinated C_6 - C_{24} -aryl, fluorinated C_7 - C_{30} -arylalkyl, fluorinated C_7 - C_{30} -alkylaryl or C_1 - C_{12} -alkoxy,

or two or more radicals R^1 may be joined to one another in such a way that the radicals R^1 and the atoms of the cyclopentadienyl ring which connect them form a C_4 - C_{24} -ring system which may in turn be substituted,

R^2 are identical or different and are each a radical $Si(R^{12})_3$, where R^{12} are identical or different and are each a hydrogen atom or a C_1 - C_{40} group, preferably C_1 - C_{20} -alkyl, C_1 - C_{10} -fluoroalkyl, C_1 - C_{10} -alkoxy, C_6 - C_{14} -aryl, C_6 - C_{10} -fluoroaryl, C_6 - C_{10} -aryloxy, C_2 - C_{10} -alkenyl, C_7 - C_{40} -arylalkyl, C_7 - C_{40} -alkylaryl or C_8 - C_{40} -arylalkenyl,

or R^2 is a C_1 - C_{30} group, preferably C_1 - C_{25} -alkyl such as methyl, ethyl, tert-butyl, cyclohexyl or octyl, C_2 - C_{25} -alkenyl, C_3 - C_{15} -alkylalkenyl, C_6 - C_{24} -aryl, C_5 - C_{24} -heteroaryl, C_7 - C_{30} -arylalkyl, C_7 - C_{30} -alkylaryl, fluorinated C_1 - C_{25} -alkyl, fluorinated C_6 - C_{24} -aryl, fluorinated C_7 - C_{30} -arylalkyl, fluorinated C_7 - C_{30} -alkylaryl or C_1 - C_{12} -alkoxy,

or two or more radicals R^2 may be joined to one another in such a way that the radicals R^2 and the atoms of the cyclopentadienyl ring which connect them form a C_4 - C_{24} ring system which may in turn be substituted,

4

- X is a halogen atom, in particular chlorine,
- n is from 1 to 5 when $k = 0$, and n is from 0 to 4 when $k = 1$,
- 5 n' is from 1 to 5 when $k = 0$, and n' is from 0 to 4 when $k = 1$,
- m is from 1 to 4, preferably 2,
- k is zero or 1, where the metallocene is unbridged when $k = 0$
 10 and is bridged when $k = 1$, with preference being given to $k = 1$, and

B is a bridging structural element between the two
 15 cyclopentadienyl rings,

comprising the steps:

- a) reacting the compound of the formula (Ia) with a ligand
 20 exchange component

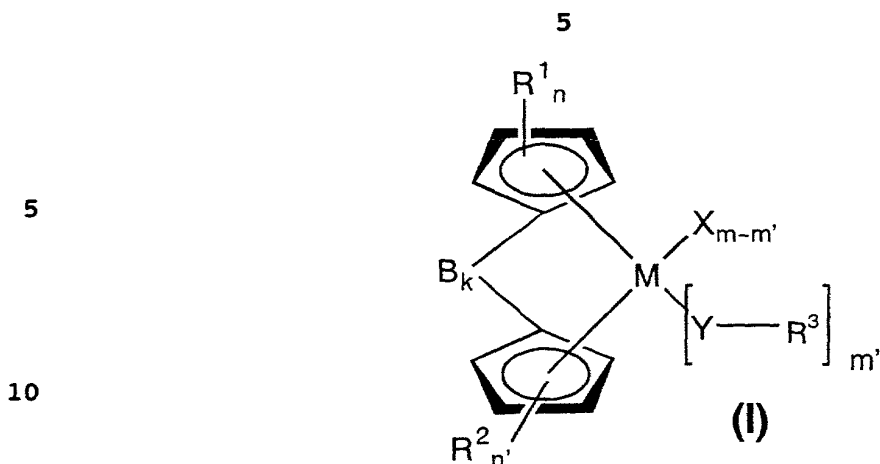


where

- 25 M^1 is a cation or a cationic fragment, in particular Li, Na, K, MgCl, MgBr, MgI, or is an ammonium cation corresponding to an amine,
- 30 R^3 is hydrogen or a C_1 - C_{40} group, preferably C_1 - C_{25} -alkyl such as methyl, ethyl, n-propyl, isopropyl tert-butyl, cyclohexyl or octyl, C_2 - C_{25} -alkenyl, C_3 - C_{15} -alkylalkenyl, C_6 - C_{24} -aryl, C_5 - C_{24} -heteroaryl such as pyridyl, furyl or quinolyl, C_7 - C_{30} -arylalkyl, C_7 - C_{30} -alkylaryl, fluorinated C_1 - C_{25} -alkyl, fluorinated C_6 - C_{24} -aryl, fluorinated
 35 C_7 - C_{30} -arylalkyl or fluorinated C_7 - C_{30} -alkylaryl,
- Y is an element of main group 6 of the Periodic Table of the Elements, in particular oxygen or sulfur, or a fragment CR^3_2 , NR^3 , $NR^3(CO)-$, $NR^3(SO_2)-$, PR^3 , $(=O)R^3$,
 40 $O(CO)-$ or $O(SO_2)-$,

to form the compound of the formula (I)

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where

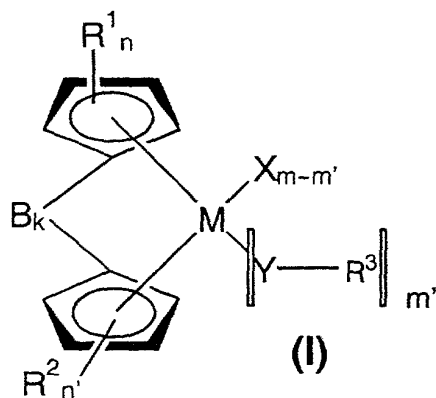
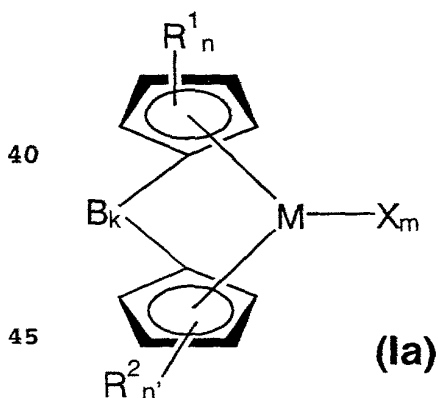
M, R¹, R², R³, X, Y, n, n', m, k, B and R¹² are as defined above and

m' is from 1 to 4, preferably 1 or 2,
with the compound of the formula M¹X, where M¹ and X are as defined above, being eliminated, in an inert solvent or solvent mixture,

- b) if desired, separating off solid residues of the formula M¹X
c) if desired, separating off the inert solvent or solvent mixture,
d) recrystallizing the compound of the formula (I) from an aprotic hydrocarbon,
e) separating the compound of the formula (I) from the mother liquor.

In the purification process of the present invention, a metallocene of the formula (Ia) is converted into a metallocene of the formula (I) and subsequently recrystallized.

In the process of the present invention, the compounds of the formulae (Ia) and (I) are



where

M is a metal of transition group III, IV, V or VI of the Periodic Table of the Elements, in particular Ti, Zr or Hf, particularly preferably zirconium,

R^1 are identical or different and are each a radical $Si(R^{12})_3$, where R^{12} are identical or different and are each a hydrogen atom or a C_1 - C_{40} group, preferably C_1 - C_{20} -alkyl, C_1 - C_{10} -fluoroalkyl, C_1 - C_{10} -alkoxy, C_6 - C_{20} -aryl, C_6 - C_{10} -fluoroaryl, C_6 - C_{10} -aryloxy, C_2 - C_{10} -alkenyl, C_7 - C_{40} -arylalkyl, C_7 - C_{40} -alkylaryl or C_8 - C_{40} -arylalkenyl,

or R^1 is a C_1 - C_{30} group, preferably C_1 - C_{25} -alkyl such as methyl, ethyl, tert-butyl, cyclohexyl or octyl, C_2 - C_{25} -alkenyl, C_3 - C_{15} -alkylalkenyl, C_6 - C_{24} -aryl, C_5 - C_{24} -heteroaryl, C_7 - C_{30} -arylalkyl, C_7 - C_{30} -alkylaryl, fluorinated C_1 - C_{25} -alkyl, fluorinated C_6 - C_{24} -aryl, fluorinated C_7 - C_{30} -arylalkyl, fluorinated C_7 - C_{30} -alkylaryl or C_1 - C_{12} -alkoxy,

or two or more radicals R^1 may be joined to one another in such a way that the radicals R^1 and the atoms of the cyclopentadienyl ring which connect them form a C_4 - C_{24} -ring system which may in turn be substituted,

R^2 are identical or different and are each a radical $Si(R^{12})_3$, where R^{12} are identical or different and are each a hydrogen atom or a C_1 - C_{40} group, preferably C_1 - C_{20} -alkyl, C_1 - C_{10} -fluoroalkyl, C_1 - C_{10} -alkoxy, C_6 - C_{14} -aryl, C_6 - C_{10} -fluoroaryl, C_6 - C_{10} -aryloxy, C_2 - C_{10} -alkenyl, C_7 - C_{40} -arylalkyl, C_7 - C_{40} -alkylaryl or C_8 - C_{40} -arylalkenyl,

or R^2 is a C_1 - C_{30} group, preferably C_1 - C_{25} -alkyl such as methyl, ethyl, tert-butyl, cyclohexyl or octyl, C_2 - C_{25} -alkenyl, C_3 - C_{15} -alkylalkenyl, C_6 - C_{24} -aryl, C_5 - C_{24} -heteroaryl, C_7 - C_{30} -arylalkyl, C_7 - C_{30} -alkylaryl, fluorinated C_1 - C_{25} -alkyl, fluorinated C_6 - C_{24} -aryl, fluorinated C_7 - C_{30} -arylalkyl, fluorinated C_7 - C_{30} -alkylaryl or C_1 - C_{12} -alkoxy,

or two or more radicals R^2 may be joined to one another in such a way that the radicals R^2 and the atoms of the cyclopentadienyl ring which connect them form a C_4 - C_{24} ring system which may in turn be substituted,

- R^3 are identical or different and are each hydrogen or a C_1-C_{40} group, preferably C_1-C_{25} -alkyl such as methyl, ethyl, n-propyl, isopropyl, tert-butyl, cyclohexyl or octyl, C_2-C_{25} -alkenyl, C_3-C_{15} -alkylalkenyl, C_6-C_{24} -aryl, C_2-C_{25} -alkenyl, C_3-C_{15} -alkylalkenyl, C_6-C_{24} -aryl,
- 5 C_5-C_{24} -heteroaryl such as pyridyl, furyl or quinolyl, C_7-C_{30} -arylalkyl, C_7-C_{30} -alkylaryl, fluorinated C_1-C_{25} -alkyl, fluorinated C_6-C_{24} -aryl, fluorinated C_7-C_{30} -arylalkyl or fluorinated C_7-C_{30} -alkylaryl,
- 10 X is a halogen atom, in particular chlorine,
- Y is an element of main group VI of the Periodic Table of the Elements, in particular oxygen or sulfur, or a fragment CR^3_2 , NR^3 , $NR^3(CO)-$, $NR^3(SO_2)-$, PR^3 , $P(=O)R^3$, $O(CO)-$ or $O(SO_2)-$,
- 15 n is from 1 to 5 when $k = 0$, and n is from 0 to 4 when $k = 1$,
- n' is from 1 to 5 when $k = 0$, and n' is from 0 to 4 when $k = 1$,
- 20 m is from 1 to 4, preferably 2,
- m' is from 1 to 4, preferably 1 or 2,
- k is zero or 1, where the metallocene is unbridged when $k=0$ and is bridged when $k=1$, with preference being given to $k=1$, and
- 25 B is a bridging structural element between the two cyclopentadienyl rings.
- 30 Examples of B are $M^3R^{13}R^{14}$ groups, where M^3 is carbon, silicon, germanium or tin and R^{13} and R^{14} are identical or different and are each a C_1-C_{20} -hydrocarbon-containing group such as C_1-C_{10} -alkyl, C_6-C_{14} -aryl or trimethylsilyl. B is preferably CH_2 , CH_2CH_2 , $CH(CH_3)CH_2$, $CH(C_4H_9)C(CH_3)_2$, $C(CH_3)_2$, $(CH_3)_2Si$, $(CH_3)_2Ge$, $(CH_3)_2Sn$,
- 35 $(C_6H_5)_2Si$, $(C_6H_5)(CH_3)Si$, $Si(CH_3)(SiR^{20}R^{21}R^{22})$, $(C_6H_5)_2Ge$, $(C_6H_5)_2Sn$, $(CH_2)_4Si$, $CH_2Si(CH_3)_2$, o- C_6H_4 or 2,2'-(C_6H_4)₂, where R^{20} , R^{21} , R^{22} are identical or different and are each a C_1-C_{20} -hydrocarbon-containing group such as C_1-C_{10} -alkyl or C_6-C_{14} -aryl. It is also possible for B together with one or more radicals R^1 and/or R^2 to
- 40 form a monocyclic or polycyclic ring system.

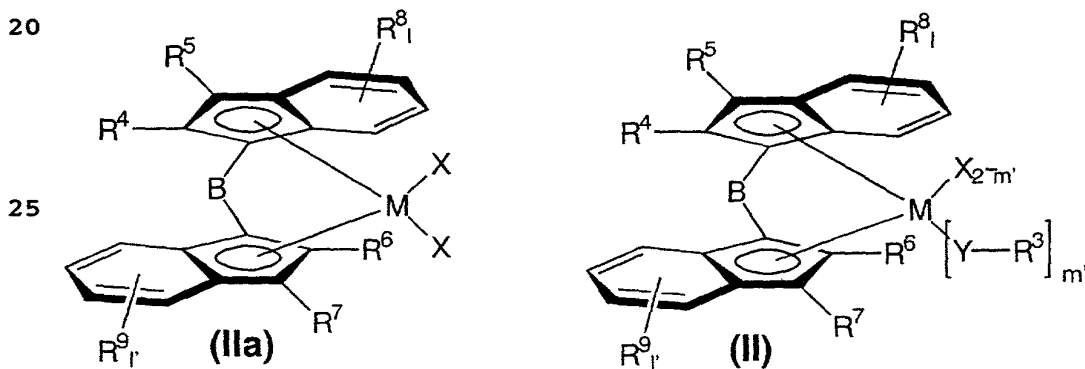
In the purification process of the present invention, metallocene halides of the formula (Ia) are reacted with a ligand exchange component to convert them directly in one reaction step into

45 metallocenes of the formula (I) which, owing to their good

solubility, are obtained in a high space-time yield and in the required purity by crystallization.

Preference is given to a purification process in which a bridged
5 metallocene of the formula (I) is formed from a bridged
metallocene of the formula (Ia), in particular a bridged
metallocene in which k is 1 and one or both cyclopentadienyl
rings are substituted in such a way that they form an indenyl
ring. The indenyl ring is preferably substituted, in particular
10 in the 2 position, 4 position, 2,4,5 positions, 2,4,6 positions,
2,4,7 positions or 2,4,5,6 positions, by C₁-C₂₀ groups such as
C₁-C₁₈-alkyl or C₆-C₁₈-aryl, where two or more substituents of the
indenyl ring may also together form a ring system.

15 Particular preference is given to a purification process in which
a bridged metallocene of the formula (IIa) is converted into a
bridged metallocene of the formula (II),



30 where

M is Ti, Zr or Hf, particularly preferably zirconium,

35 R³ are identical or different and are each hydrogen or a
C₁-C₃₀ group, preferably C₁-C₁₀-alkyl such as methyl,
ethyl, n-propyl, isopropyl, tert-butyl, cyclohexyl or
octyl, C₂-C₁₆-alkenyl, C₆-C₂₄-aryl, C₅-C₂₄-heteroaryl such
as pyridyl, furyl or quinolyl, C₇-C₃₀-arylalkyl,
40 C₇-C₃₀-alkylaryl, fluorinated C₆-C₂₄-aryl, fluorinated
C₇-C₃₀-arylalkyl or fluorinated C₇-C₃₀-alkylaryl,

45 R⁴, R⁶ are identical or different and are each a hydrogen atom
or a C₁-C₂₀ group, preferably C₁-C₁₈-alkyl such as methyl,
ethyl, n-butyl, cyclohexyl or octyl, C₂-C₁₀-alkenyl,
C₃-C₁₅-alkylalkenyl, C₆-C₁₈-aryl, C₅-C₁₈-heteroaryl such as
pyridyl, furyl or quinolyl, C₇-C₂₀-arylalkyl,
C₇-C₂₀-alkylaryl, fluorinated C₁-C₁₂-alkyl, fluorinated

C₆-C₁₈-aryl, fluorinated C₇-C₂₀-arylalkyl or fluorinated C₇-C₂₀-alkylaryl,

- 5 R⁵, R⁷ are identical or different and are each a hydrogen atom or a C₁-C₂₀ group, preferably C₁-C₁₈-alkyl such as methyl, ethyl, n-butyl, cyclohexyl or octyl, C₂-C₁₀-alkenyl, C₃-C₁₅-alkylalkenyl, C₆-C₁₈-aryl, C₅-C₁₈-heteroaryl such as pyridyl, furyl or quinolyl, C₇-C₂₀-arylalkyl, C₇-C₂₀-alkylaryl, fluorinated C₁-C₁₂-alkyl, fluorinated C₆-C₁₈-aryl, fluorinated C₇-C₂₀-arylalkyl or fluorinated C₇-C₂₀-alkylaryl,
- 10
- 15 R⁸ and R⁹ are identical or different and are each a hydrogen atom, a halogen atom or a C₁-C₂₀ group, preferably a linear or branched C₁-C₁₈-alkyl group such as methyl, ethyl, tert-butyl, cyclohexyl or octyl, C₂-C₁₀-alkenyl, C₃-C₁₅-alkylalkenyl, a C₆-C₁₈-aryl group which may be substituted, in particular phenyl, tolyl, xylyl, tert-butylphenyl, ethylphenyl, di-tert-butylphenyl, naphthyl, acenaphthyl, phenanthrenyl or anthracenyl, C₅-C₁₈-heteroaryl such as pyridyl, furyl or quinolyl, C₇-C₂₀-arylalkyl, C₇-C₂₀-alkylaryl, fluorinated C₁-C₁₂-alkyl, fluorinated C₆-C₁₈-aryl, fluorinated C₇-C₂₀-arylalkyl or fluorinated C₇-C₂₀-alkylaryl, and two
- 20
- 25 radicals R⁸ or R⁹ may form a monocyclic or polycyclic ring system which may in turn be substituted,
- X is a halogen atom, in particular chlorine,
- 30 Y is an element of main group VI of the Periodic Table of the Elements, in particular oxygen or sulfur, or a fragment CR³₂, NR³, NR³(CO)-, NR³(SO₂)-, PR³, P(=O)R³, O(CO)- or O(SO₂)-,
- 35 l, l' are identical or different and are each an integer from zero to 4, preferably 1 or 2, particularly preferably 1,
- m' is 1 or 2,
- 40 B is a bridging structural element between the two indenyl radicals.

Examples of B are M³R¹³R¹⁴ groups, where M³ is carbon, silicon, germanium or tin, preferably carbon or silicon, and R¹³ and R¹⁴

- 45 are identical or different and are each hydrogen or a C₁-C₂₀-hydrocarbon-containing group such as C₁-C₁₀-alkyl, C₆-C₁₄-aryl or trimethylsilyl. B is preferably CH₂, CH₂CH₂,

10

CH(CH₃)CH₂, CH(C₄H₉)C(CH₃)₂, C(CH₃)₂, (CH₃)₂Si, (CH₃)₂Ge, (CH₃)₂Sn, (C₆H₅)₂C, (C₆H₅)₂Si, (C₆H₅)(CH₃)Si, Si(CH₃)(SiR²⁰R²¹R²²), (C₆H₅)₂Ge, (C₆H₅)₂Sn, (CH₂)₄Si, CH₂Si(CH₃)₂, o-C₆H₄ or 2,2'-(C₆H₄)₂, where R²⁰, R²¹, R²² are identical or different and are each a

- 5 C₁-C₂₀-hydrocarbon-containing group such as C₁-C₁₀-alkyl or C₆-C₁₄-aryl.

Very particular preference is given to a purification process in which a bridged metallocene of the formula (IIa) is converted
10 into a bridged metallocene of the formula (II), where

M is zirconium,

- 15 R³ are identical or different and are each hydrogen or a C₁-C₃₀ group, preferably C₁-C₁₀-alkyl such as methyl, ethyl, n-propyl, isopropyl, tert-butyl, cyclohexyl or octyl, C₂-C₁₂-alkenyl, C₆-C₂₄-aryl, C₅-C₂₄-heteroaryl such as pyridyl, furyl or quinolyl, C₇-C₃₀-arylalkyl, C₇-C₃₀-alkylaryl, fluorinated C₆-C₂₄-aryl, fluorinated
20 C₇-C₃₀-arylalkyl or fluorinated C₇-C₃₀-alkylaryl,

- R⁴, R⁶ are identical or different and are each a hydrogen atom or a C₁-C₁₂-alkyl group, preferably an alkyl group such as methyl, ethyl, n-butyl or octyl, particularly
25 preferably methyl or ethyl,

R⁵, R⁷ are hydrogen atoms,

- 30 R⁸ and R⁹ are identical or different and are each a hydrogen atom, a halogen atom or a C₁-C₂₀ group, preferably a linear or branched C₁-C₈-alkyl group such as methyl, ethyl, tert-butyl, cyclohexyl or octyl, C₂-C₆-alkenyl, C₃-C₆-alkylalkenyl, a C₆-C₁₈-aryl group which may be substituted, in particular phenyl, tolyl, xylyl, tert-butylphenyl, ethylphenyl, di-tert-butylphenyl, naphthyl, acenaphthyl, phenanthrenyl or anthracenyl, C₅-C₁₈-heteroaryl such as pyridyl, furyl or quinolyl, C₇-C₁₂-arylalkyl, C₇-C₁₂-alkylaryl, fluorinated
35 C₁-C₈-alkyl, fluorinated C₆-C₁₈-aryl, fluorinated C₇-C₁₂-arylalkyl or fluorinated C₇-C₁₂-alkylaryl,
40

X is chlorine,

45

11

- Y is an element of main group VI of the Periodic Table of the Elements, in particular oxygen or sulfur, or a fragment CR^3_2 , NR^3 , $NR^3(CO)-$, $NR^3(SO_2)-$, PR^3 , $P(=O)R^3$, $O(CO)-$ or $O(SO_2)-$,
- 5 1, 1' are identical or different and are each an integer from zero to 4, preferably 1 or 2, particularly preferably 1,
- m' is 1 or 2, preferably 1, and
- 10 B is a bridging structural element between the two indenyl radicals and is preferably $(CH_3)_2Si$, $(CH_3)_2Ge$, $(C_6H_5)_2Si$, $(C_6H_5)(CH_3)Si$, CH_2CH_2 , $CH(CH_3)CH_2$, $CH(C_4H_9)C(CH_3)_2$, CH_2 , $C(CH_3)_2$, $(C_6H_5)_2C$, particularly preferably $(CH_3)_2Si$, CH_2 and CH_2CH_2 .
- 15

When Y = oxygen and R^3 is alkenyl, individual CH_2 units in the alkenyl radical can be replaced by $C=O$, $C(O)O$ or $C(O)NR^3$.

- 20 The metallocenes of the formulae I and II obtained in the purification process of the present invention display a significantly better solubility in inert organic solvents than do the corresponding metallocenes of the formulae (Ia) and (IIa). For the purposes of the present invention, a significantly better
- 25 solubility means that the molar concentrations in organic solvents are at least doubled, preferably more than quadrupled and very particularly preferably increased by a factor of more than eight.
- 30 As inert organic solvents for metallocenes, use is made of the usual aliphatic or aromatic hydrocarbons and also halogen-containing, oxygen-containing or nitrogen-containing hydrocarbons. Nonlimiting examples of the individual classes of solvent are heptane, toluene, dichlorobenzene, methylene
- 35 chloride, tetrahydrofuran or triethylamine.

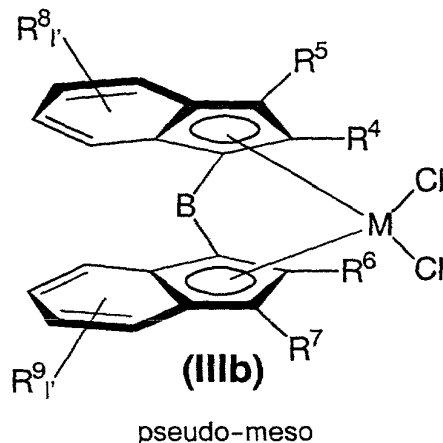
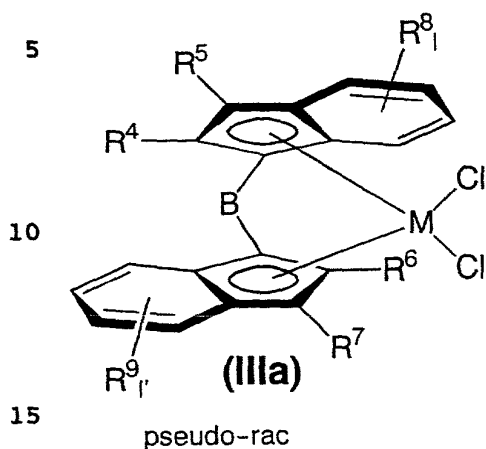
The purification process of the present invention is preferably carried out using metallocenes of the formulae (Ia) and (IIa), i.e. racemic metallocene dichlorides as are mentioned in

- 40 EP-A-0485823, EP-A-0549900, EP-A-0576970, WO 98/22486 and WO 98/40331. These are hereby incorporated by reference into the present description.

- However, it is also possible to use any mixtures of the racemic
- 45 metallocene dichloride of the formula (IIIa) with the corresponding meso-metallocene dichloride of the formula (IIIb),

12

where the symbols and indices are defined as under formula (IIa),
in the purification process of the present invention.



The metallocenes of the formulae (Ia) and (IIa) used in the
purification process of the present invention, preferably the
20 metallocenes of the formula (IIa), can be used in the form in
which they are obtained directly from the metallocene synthesis
together with the inorganic, organometallic and organic
by-products, or in the form in which they can be obtained after
separating off a large part of the by-products by one of the
25 abovementioned known purification methods.

Illustrative but nonlimiting examples of metallocenes of the
formula (Ia) or (IIa) which can be used in the purification
process of the present invention are:

- 30 dimethylsilanediylbis(indenyl)zirconium dichloride
dimethylsilanediylbis(2-methylindenyl)zirconium dichloride
methylidenebis(2-methylindenyl)zirconium dichloride
isopropylidenebis(2-methylindenyl)zirconium dichloride
35 dimethylsilanediylbis(2-methylbenzoidindenyl)zirconium dichloride
dimethylsilanediylbis(4-naphthylindenyl)zirconium dichloride
dimethylsilanediylbis(2-methyl-4-(1-naphthyl)indenyl)zirconium
dichloride
methylidenebis(2-methyl-4-(1-naphthyl)indenyl)zirconium
40 dichloride
isopropylidenebis(2-methyl-4-(1-naphthyl)indenyl)zirconium
dichloride
dimethylsilanediylbis(2-methyl-4-(2-naphthyl)indenyl)zirconium
dichloride
45 dimethylsilanediylbis(2-methyl-4-phenylindenyl)zirconium
dichloride
methylidenebis(2-methyl-4-phenylindenyl)zirconium dichloride

- isopropylidenebis(2-methyl-4-phenylindenyl)zirconium dichloride
dimethylsilanediylbis(2-methyl-4-t-butylindenyl)zirconium
dichloride
dimethylsilanediylbis(2-methyl-4-isopropylindenyl)zirconium
5 dichloride
dimethylsilanediylbis(2-methyl-4-ethylindenyl)zirconium
dichloride
dimethylsilanediylbis(2,4-dimethylindenyl)zirconium dichloride
dimethylsilanediylbis(2-ethylindenyl)zirconium dichloride
10 dimethylsilanediylbis(2-ethyl-4-ethylindenyl)zirconium dichloride
dimethylsilanediylbis(2-ethyl-4-phenylindenyl)zirconium
dichloride
dimethylsilanediylbis(2-methyl-4,5-benzoindenyl)zirconium
dichloride
15 methylidenebis(2-methyl-4,5-benzoindenyl)zirconium dichloride
isopropylidenebis(2-methyl-4,5-benzoindenyl)zirconium dichloride
dimethylsilanediylbis(2-methyl-4,6-diisopropylindenyl)zirconium
dichloride
dimethylsilanediylbis(2-methyl-4,5-diisopropylindenyl)zirconium
20 dichloride
dimethylsilanediylbis(2,4,6-trimethylindenyl)zirconium dichloride
dimethylsilanediylbis(2,5,6-trimethylindenyl)zirconium dichloride
dimethylsilanediylbis(2,4,7-trimethylindenyl)zirconium dichloride
dimethylsilanediylbis(2-methyl-5-isobutylindenyl)zirconium
25 dichloride
dimethylsilanediylbis(2-methyl-5-t-butylindenyl)zirconium
dichloride
methyl(phenyl)silanediylbis(2-methyl-4-phenylindenyl)zirconium
dichloride
30 methyl(phenyl)silanediylbis(2-methyl-4,6-diisopropylindenyl)-
zirconium dichloride
methyl(phenyl)silanediylbis(2-methyl-4-isopropylindenyl)zirconium
dichloride
methyl(phenyl)silanediylbis(2-methyl-4,5-benzoindenyl)zirconium
35 dichloride
methyl(phenyl)silanediylbis(2-methylindenyl)zirconium dichloride
methyl(phenyl)silanediylbis(2-methyl-5-isobutylindenyl)zirconium
dichloride
1,2-ethanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride
40 1,4-butanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride
1,2-ethanediylbis(2-methyl-4,6-diisopropylindenyl)zirconium
dichloride
1,4-butanediylbis(2-methyl-4-isopropylindenyl)zirconium
dichloride
45 1,4-butanediylbis(2-methyl-4,5-benzoindenyl)zirconium dichloride
1,2-ethanediylbis(2-methyl-4,5-benzoindenyl)zirconium dichloride
1,2-ethanediylbis(2,4,7-trimethylindenyl)zirconium dichloride

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- 1,2-ethanediylbis(2-methylindenyl)zirconium dichloride
 1,4-butanediylbis(2-methylindenyl)zirconium dichloride
 [4-(η^5 -cyclopentadienyl)-4,6,6-trimethyl(η^5 -4,5-tetrahydropentalene)]zirconium dichloride
- 5 [4-(η^5 -3'-trimethylsilylcyclopentadienyl)-4,6,6-trimethyl(η^5 -4,5-tetrahydropentalene)]zirconium dichloride
 [4-(η^5 -3'-isopropylcyclopentadienyl)-4,6,6-trimethyl-(η^5 -4,5-tetrahydropentalene)]zirconium dichloride
 [4-(η^5 -cyclopentadienyl)-4,7,7-trimethyl-(η^5 -4,5,6,7-tetrahydroindenyl)]zirconium dichloride
- 10 [4-(η^5 -3'-tert-butylcyclopentadienyl)-4,7,7-trimethyl(η^5 -4,5,6,7-tetrahydroindenyl)]zirconium dichloride
 4-(η^5 -3'-methylcyclopentadienyl)-4,7,7-trimethyl-(η^5 -4,5,6,7-tetrahydroindenyl)]zirconium dichloride
- 15 4-(η^5 -3'-trimethylsilylcyclopentadienyl)-2-trimethylsilyl-4,7,7-trimethyl-(η^5 -4,5,6,7-tetrahydroindenyl)]zirconium dichloride
 dimethylsilanediylbis(tetrahydroindenyl)zirconium dichloride
 isopropylidenebisindenylzirconium dichloride
 isopropylidenecyclopentadienyl-9-fluorenylzirconium dichloride
- 20 isopropylidenecyclopentadienylindenylzirconium dichloride
 diphenylmethylidene(cyclopentadienyl)-(9-fluorenyl)zirconium dichloride
 diphenylmethylidene(3-methylcyclopentadienyl)-(9-fluorenyl)-zirconium dichloride
- 25 diphenylmethylidene(3-isopropylcyclopentadienyl)-(9-fluorenyl)-zirconium dichloride
 diphenylmethylidene(3-tert-butylcyclopentadienyl)-(9-fluorenyl)-zirconium dichloride
 dimethylsilanediylcyclopentadienyl-9-fluorenylzirconium
- 30 dichloride
 diphenylsilanediylcyclopentadienyl-9-fluorenylzirconium dichloride
 dimethylsilanediylbis(2-methyl-4-(tert-butylphenylindenyl))-zirconium dichloride
- 35 dimethylsilanediylbis(2-methyl-4-(4-trifluoromethylphenylindenyl))zirconium dichloride
 dimethylsilanediylbis(2-methyl-4-(4-methoxyphenylindenyl))-zirconium dichloride
 dimethylsilanediylbis(2-ethyl-4-(4-methylphenylindenyl))zirconium
- 40 dichloride
 dimethylsilanediylbis(2-ethyl-4-(4-ethylphenylindenyl))zirconium dichloride
 dimethylsilanediylbis(2-ethyl-4-(4-trifluoromethylphenylindenyl))-zirconium dichloride
- 45 dimethylsilanediylbis(2-ethyl-4-(4-methoxyphenylindenyl))zirconium dichloride

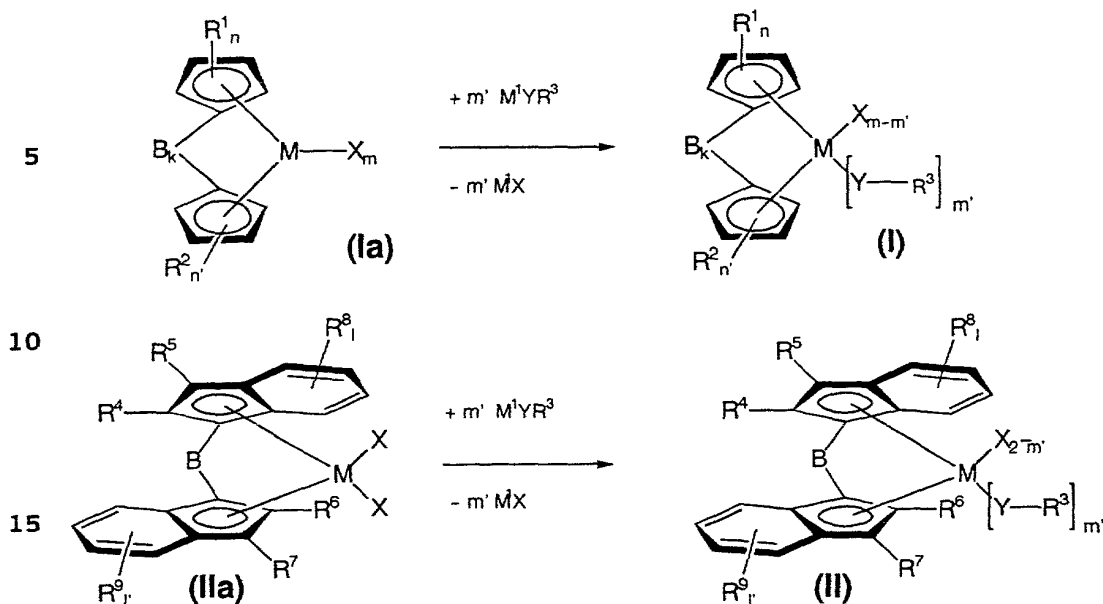
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- dimethylsilanediylbis(2-methyl-4-(4'-tert-butylphenyl)indenyl)-
zirconium dichloride
- dimethylsilanediylbis(2-methyl-4-(3',5'-di-tert-butylphenyl)-
indenyl)zirconium dichloride
- 5 methylidenebis(2-methyl-4-(4'-tert-butylphenyl)indenyl)zirconium
dichloride
- isopropylidenebis(2-methyl-4-(4'-tert-butylphenyl)indenyl)-
zirconium dichloride
- dimethylsilanediylbis(2-methyl-4-(4'-methylphenyl)indenyl)-
- 10 zirconium dichloride
- dimethylsilanediylbis(2-methyl-4-(4'-ethylphenyl)indenyl)-
zirconium dichloride
- dimethylsilanediylbis(2-methyl-4-(4'-n-propylphenyl)indenyl)-
zirconium dichloride
- 15 dimethylsilanediylbis(2-methyl-4-(4'-isopropylphenyl)indenyl)-
zirconium dichloride
- dimethylsilanediylbis(2-methyl-4-(4'-n-butylphenyl)indenyl)-
zirconium dichloride
- dimethylsilanediylbis(2-methyl-4-(4'-hexylphenyl)indenyl)-
- 20 zirconium dichloride
- dimethylsilanediylbis(2-methyl-4-(4'-sec-butylphenyl)indenyl)-
zirconium dichloride
- dimethylsilanediylbis(2-ethyl-4-phenyl)indenyl)zirconium
dichloride
- 25 dimethylsilanediylbis(2-ethyl-4-(4'-methylphenyl)indenyl)-
zirconium dichloride
- dimethylsilanediylbis(2-ethyl-4-(4'-ethylphenyl)indenyl)zirconium
dichloride
- dimethylsilanediylbis(2-ethyl-4-(4'-n-propylphenyl)indenyl)-
- 30 zirconium dichloride
- dimethylsilanediylbis(2-ethyl-4-(4'-isopropylphenyl)indenyl)-
zirconium dichloride
- dimethylsilanediylbis(2-ethyl-4-(4'-n-butylphenyl)indenyl)-
zirconium dichloride
- 35 dimethylsilanediylbis(2-ethyl-4-(4'-hexylphenyl)indenyl)zirconium
dichloride
- dimethylsilanediylbis(2-ethyl-4-(4'-pentylphenyl)indenyl)-
zirconium dichloride
- dimethylsilanediylbis(2-ethyl-4-(4'-cyclohexylphenyl)indenyl)-
- 40 zirconium dichloride
- dimethylsilanediylbis(2-ethyl-4-(4'-sec-butylphenyl)indenyl)-
zirconium dichloride
- dimethylsilanediylbis(2-ethyl-4-(4'-tert-butylphenyl)indenyl)-
zirconium dichloride
- 45 dimethylsilanediylbis(2-ethyl-4-(3',5'-di-tert-butylphenyl)-
indenyl)zirconium dichloride

- methylidenebis(2-ethyl-4-(4'-tert-butylphenyl)indenyl)zirconium dichloride
isopropylidenebis(2-ethyl-4-(4'-tert-butylphenyl)indenyl)-zirconium dichloride
- 5 dimethylsilanediylbis(2-n-propyl-4-phenyl)indenyl)zirconium dichloride
dimethylsilanediylbis(2-n-propyl-4-(4'-methylphenyl)indenyl)-zirconium dichloride
dimethylsilanediylbis(2-n-propyl-4-(4'-ethylphenyl)indenyl)-zirconium dichloride
- 10 dimethylsilanediylbis(2-n-propyl-4-(4'-n-propylphenyl)indenyl)-zirconium dichloride
dimethylsilanediylbis(2-n-propyl-4-(4'-isopropylphenyl)indenyl)-zirconium dichloride
- 15 dimethylsilanediylbis(2-n-propyl-4-(4'-n-butylphenyl)indenyl)-zirconium dichloride
dimethylsilanediylbis(2-n-propyl-4-(4'-hexylphenyl)indenyl)-zirconium dichloride
dimethylsilanediylbis(2-n-propyl-4-(4'-cyclohexylphenyl)indenyl)-zirconium dichloride
- 20 dimethylsilanediylbis(2-n-propyl-4-(4'-sec-butylphenyl)indenyl)-zirconium dichloride
dimethylsilanediylbis(2-n-propyl-4-(4'-tert-butylphenyl)indenyl)-zirconium dichloride
- 25 dimethylsilanediylbis(2-n-propyl-4-(3',5'-di-tert-butylphenyl)indenyl)zirconium dichloride
methylidenebis(2-n-propyl-4-(4'-tert-butylphenyl)indenyl)-zirconium dichloride
isopropylidenebis(2-n-propyl-4-(4'-tert-butylphenyl)indenyl)-zirconium dichloride
- 30 dimethylsilanediylbis(2-n-butyl-4-phenyl)indenyl)zirconium dichloride
dimethylsilanediylbis(2-n-butyl-4-(4'-methylphenyl)indenyl)-zirconium dichloride
- 35 dimethylsilanediylbis(2-n-butyl-4-(4'-ethylphenyl)indenyl)-zirconium dichloride
dimethylsilanediylbis(2-n-butyl-4-(4'-n-propylphenyl)indenyl)-zirconium dichloride
dimethylsilanediylbis(2-n-butyl-4-(4'-isopropylphenyl)indenyl)-zirconium dichloride
- 40 dimethylsilanediylbis(2-n-butyl-4-(4'-n-butylphenyl)indenyl)-zirconium dichloride
dimethylsilanediylbis(2-n-butyl-4-(4'-hexylphenyl)indenyl)-zirconium dichloride
- 45 dimethylsilanediylbis(2-n-butyl-4-(4'-cyclohexylphenyl)indenyl)-zirconium dichloride

- dimethylsilanediylbis(2-n-butyl-4-(4'-sec-butylphenyl)indenyl)-
zirconium dichloride
- dimethylsilanediylbis(2-n-butyl-4-(4'-tert-butylphenyl)indenyl)-
zirconium dichloride
- 5 dimethylsilanediylbis(2-hexyl-4-phenyl)indenyl)zirconium
dichloride
- dimethylsilanediylbis(2-hexyl-4-(4'-methylphenyl)indenyl)-
zirconium dichloride
- dimethylsilanediylbis(2-hexyl-4-(4'-ethylphenyl)indenyl)zirconium
10 dichloride
- dimethylsilanediylbis(2-hexyl-4-(4'-n-propyl-phenyl)-indenyl)-
zirconium dichloride
- Dimethylsilanediylbis(2-hexyl-4-(4'-isopropylphenyl)indenyl)-
zirconium dichloride
- 15 dimethylsilanediylbis(2-hexyl-4-(4'-n-butylphenyl)indenyl)-
zirconium dichloride
- dimethylsilanediylbis(2-hexyl-4-(4'-hexylphenyl)indenyl)zirconium
dichloride
- dimethylsilanediylbis(2-hexyl-4-(4'-cyclohexylphenyl)indenyl)-
20 zirconium dichloride
- dimethylsilanediylbis(2-hexyl-4-(4'-sec-butylphenyl)indenyl)-
zirconium dichloride
- dimethylsilanediylbis(2-hexyl-4-(4'-tert-butylphenyl)indenyl)-
zirconium dichloride
- 25 dimethylgermandiylbis(2-ethyl-4-(4'-tert-butylphenyl)indenyl)-
zirconium dichloride
- dimethylgermandiylbis(2-methyl-4-(4'-tert-butylphenyl)indenyl)-
zirconium dichloride
- ethylidenebis(2-ethyl-4-phenyl)indenyl)zirconium dichloride
- 30 ethylidenebis(2-ethyl-4-(4'-tert-butylphenyl)indenyl)zirconium
dichloride
- ethylidenebis(2-n-propyl-4-(4'-tert-butylphenyl)indenyl)zirconium
dichloride
- ethylidenebis(2-methyl-4-(4'-tert-butylphenyl)indenyl)zirconium
35 dichloride
- methylethylidenebis(2-ethyl-4-(4'-tert-butylphenyl)indenyl)-
zirconium dichloride
- dimethylsilanediyl(2-methylazapentalene)(2-methylindenyl)-
zirconium dichloride
- 40 dimethylsilanediyl(2-methylazapentalene)(2-methyl-
4-phenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methylazapentalene)(2-methyl-
4,5-benzoidindenyl)zirconium dichloride
- dimethylsilanediyl(2-methylazapentalene)(2-ethyl-
4-(4'-tert-butylphenylindenyl)zirconium dichloride
- 45 dimethylsilanediyl(2-methylazapentalene)(2-methyl-
4-(4'-tert-butylphenyl)indenyl)zirconium dichloride

- dimethylsilanediyl(2-methylazapentalene)(2-n-propyl-4-(4'-tert-butylphenyl)indenyl)zirconium dichloride
 dimethylsilanediyl(2-ethylazapentalene)(2-methyl-4-phenylindenyl)zirconium dichloride
 5 dimethylsilanediyl(2-ethylazapentalene)(2-methyl-4-phenylindenyl)zirconium dichloride
 dimethylsilanediyl(2-ethylazapentalene)(2-methyl-4,5-benzindenyl)zirconium dichloride
 dimethylsilanediyl(2-ethylazapentalene)(2-ethyl-4-(4'-tert-butylphenyl)indenyl)zirconium dichloride
 10 dimethylsilanediyl(2-ethylazapentalene)(2-methyl-4-(4'-tert-butylphenyl)indenyl)zirconium dichloride
 dimethylsilanediyl(2-ethylazapentalene)(2-n-propyl-4-(4'-tert-butylphenyl)indenyl)zirconium dichloride
 15 dimethylsilanediyl(2-methylthiapentalene)(2-methylindenyl)-zirconium dichloride
 dimethylsilanediyl(2-methylthiapentalene)(2-methyl-4-phenylindenyl)zirconium dichloride
 dimethylsilanediyl(2-methylthiapentalene)(2-methyl-4,5-benzindenyl)zirconium dichloride
 20 dimethylsilanediyl(2-methylthiapentalene)(2-ethyl-4-(4'-tert-butylphenyl)indenyl)zirconium dichloride
 dimethylsilanediyl(2-methylthiapentalene)(2-n-propyl-4-(4'-tert-butylphenyl)indenyl)zirconium dichloride
 25 dimethylsilanediyl(2-ethylthiapentalene)(2-methylindenyl)-zirconium dichloride
 dimethylsilanediyl(2-ethylthiapentalene)(2-methyl-4-phenylindenyl)zirconium dichloride
 dimethylsilanediyl(2-ethylthiapentalene)(2-methyl-4,5-benzindenyl)zirconium dichloride
 30 dimethylsilanediyl(2-ethylthiapentalene)(2-ethyl-4-(4'-tert-butylphenyl)indenyl)zirconium dichloride
 dimethylsilanediyl(2-ethylthiapentalene)(2-n-propyl-4-(4'-tert-butylphenyl)indenyl)zirconium dichloride
 35
- In the purification process of the present invention, at least one metallocene halide of the formula (Ia) or (IIa) is reacted with at least one ligand exchange component M^1YR^3 , forming the metallocenes of the formula (I) or (II). Here, the ligand
- 40 exchange component serves to introduce the ligand $Y-R^3$. The metallocenes of the formula (I) and (II) can, owing to their good solubility, be obtained in the required quality and in good space-time yields by crystallization. The salts formed in the ligand exchange can, for example, be removed by known filtration
- 45 techniques.



20 Here, M^1 is a cation or a cationic fragment such as Li, Na, K, MgCl, MgBr, MgI or the ammonium cation corresponding to an amine, and the other radicals are as defined above.

The replacement of the halide ligands in metallocene halides by
 25 other ligands is known in principle. In particular, the replacement of chloride ligands by other anions which can act as ligands on the zirconocene has been described (e.g. Replacement of chloride by aryloxy: T. Repo et al., J. Organomet. Chem. 541 (1997), 363, and references cited therein; B. Khera et al.,
 30 Polyhedron 3 (5), (1984), 611, and references cited therein; B. Khera et al., Polyhedron 2 (11), (1983), 1177; Replacement of chloride by alkyl or aryl: E.W. Abel, F.G. Stone, G. Wilkinson, Comprehensive Organometallic Chemistry II, Volume 4, Elsevier Science Ltd., p. 573, 575, 577; Replacement of chloride by
 35 carboxylate: E.W. Abel, F.G. Stone, G. Wilkinson, Comprehensive Organometallic Chemistry II, Volume 4, Elsevier Science Ltd., p. 525; Replacement of chloride by various further anions: E.W. Abel, F.G. Stone, G. Wilkinson, Comprehensive Organometallic Chemistry II, Volume 4, Elsevier Science Ltd., chapter 5, 10 and
 40 11).

In the purification process of the present invention, metallocene halides are firstly reacted with salts of the formula M^1-Y-R^3 in an inert solvent or solvent mixture at from 0°C to $+200^\circ\text{C}$,
 45 preferably from 40°C to 140°C , particularly preferably from 60°C to 110°C .

20

The compound M^1-Y-R^3 used in the purification process of the present invention can be prepared, for example, by deprotonation of the acid compound $H-Y-R^3$ using a suitable base, for example butyllithium, methyllithium, sodium hydride, potassium hydride, 5 sodium, potassium, Grignard compounds or amines, in an inert solvent or solvent mixture, or M^1-Y-R^3 is a commercially available organometallic compound such as an organolithium compound, for example methyllithium, an organoaluminum compound, for example trimethylaluminum, or a Grignard compound, for example 10 benzylmagnesium chloride.

Nonlimiting examples of suitable solvents are hydrocarbons which may be halogenated, e.g. benzene, toluene, xylene, mesitylene, ethylbenzene, chlorobenzene, dichlorobenzene, fluorobenzene, 15 decalin, tetralin, pentane, hexane, cyclohexane, ethers such as diethyl ether, di-n-butyl ether, tert-butyl methyl ether (MTBE), tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), anisole, triglyme, dioxane, amides such as dimethylformamide (DMF), dimethylacetamide, N-methyl-2-pyrrolidinone (NMP), sulfoxides 20 such as dimethyl sulfoxide (DMSO), phosphoramides such as hexamethylphosphoramide, urea derivatives such as 1,3-dimethyltetrahydro-2(1H)-pyrimidinone, ketones such as acetone, ethyl methyl ketone, esters such as ethyl acetate, nitriles such as acetonitrile and also any mixtures of these. 25 Preference is given to solvents or solvent mixtures in which the subsequent reaction with the metallocene dichloride can likewise be carried out. Nonlimiting examples of such solvents are toluene, hexane, heptane, xylene, tetrahydrofuran (THF), dimethoxyethane (DME), toluene/THF, heptane/DME and toluene/DME.

30 The compounds of the type $H-Y-R^3$ are, for example, alcohols, phenols, carboxylic acids, alkylsulfonic and arylsulfonic acids, primary and secondary amines, primary and secondary anilines, carboxamides, sulfonamides, dialkylphosphines or diarylphosphines 35 and dialkylphosphine oxides or diarylphosphine oxides. Examples of CH -acid, enolisable compounds $H-Y-R^3$ are malonic esters, cyanoacetic esters, acetoacetic esters, 1,3-diketones, enolisable esters and enolisable ketones.

40 Compounds of the type $H-Y-R^3$ preferably contain only one functional group $H-Y$ and the radical R^3 is as defined above.

Illustrative but nonlimiting examples of compounds of the formula $H-Y-R^3$ which can be used according to the present invention are:

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21

- 2,4-di-tert-butylphenol; 2,6-di-tert-butylphenol;
 3,5-di-tert-butylphenol; 2,6-di-sec-butylphenol;
 2,4-dimethylphenol; 2,3-dimethylphenol; 2,5-dimethylphenol;
 2,6-dimethylphenol; 3,4-dimethylphenol; 3,5-dimethylphenol;
 5 phenol; 2-methylphenol; 3-methylphenol; 4-methylphenol;
 2-ethylphenol; 3-ethylphenol; 4-ethylphenol; 2-sec-butylphenol;
 2-tert-butylphenol; 3-tert-butylphenol; 4-sec-butylphenol;
 4-tert-butylphenol; 2-isopropyl-5-methylphenol;
 4-isopropyl-3-methylphenol; 5-isopropyl-2-methylphenol;
 10 5-isopropyl-3-methylphenol; 2,4-bis(2-methyl-2-butyl)phenol;
 2,6-di-tert-butyl-4-methylphenol; 4-nonylphenol;
- 2-isopropylphenol; 3-isopropylphenol; 4-isopropylphenol;
 2-propylphenol; 4-propylphenol; 2,3,5-trimethylphenol;
 15 2,3,6-trimethylphenol; 2,4,6-trimethylphenol;
 3,4,5-trimethylphenol; 2-tert-butyl-4-methylphenol;
 2-tert-butyl-5-methylphenol; 2-tert-butyl-6-methylphenol;
 4-(2-methyl-2-butyl)phenol; 2-tert-butyl-4-ethylphenol;
 2,6-diisopropylphenol; 4-octylphenol;
 20 4-(1,1,3,3-tetramethylbutyl)phenol;
 2,6-di-tert-butyl-4-ethylphenol;
 4-sec-butyl-2,6-di-tert-butylphenol; 4-dodecylphenol;
 2,4,6-tri-tert-butylphenol; 3-(pentadecyl)phenol;
 2-methyl-1-naphthol;
- 25 1-naphthol; 2-naphthol; 1-acenaphthenol; 2-hydroxybiphenyl;
 3-hydroxybiphenyl; 4-hydroxybiphenyl; hydroxypyridines;
 hydroxyquinolines; 2-hydroxycarbazole; hydroxyquinaldines;
 8-hydroxyquinazoline; 2-hydroxyquinoxaline;
- 30 2-hydroxydibenzofuran; 2-hydroxydiphenylmethane,
 1-hydroxyisoquinolines, 5,6,7,8-tetrahydro-1-naphthol; methanol;
 ethanol; propanol; isopropanol; butanol; tert-butanol;
 isobutanol; 2-butanol; hexanol; cyclohexanol; octadecanol; benzyl
 alcohol; 2-methylbenzyl alcohol; 3-methylbenzyl alcohol;
- 35 4-methylbenzyl alcohol; aniline; N-methylaniline; o-toluidine;
 2,3-dimethylaniline; 2,4-dimethylaniline; 2,5-dimethylaniline;
 2,6-dimethylaniline; N-ethylaniline; 2-ethylaniline;
 N-ethyl-o-toluidine; N-ethyl-m-toluidine; 2-isopropylaniline;
 2-propylaniline; 2,4,6-trimethylaniline; 2-tert-butylaniline;
- 40 2,3-dimethyl-N-ethylaniline; isopropylamine; tert-butylamine;
 diethylamine; N-methylisopropylamine; N-ethylisopropylamine;
 diisopropylamine; N-methyl-tert-butylamine; N-benzylmethylamine;
 2-methylbenzylamine; 3-methylbenzylamine; 4-methylbenzylamine;
 1-phenylethylamine; 2-phenylethylamine; acetic acid; propionic
- 45 acid; butyric acid; phenylacetic acid; benzoic acid; toluic acid;
 dimethylbenzoic acid; 4-tert-butylbenzoic acid; methanesulfonic
 acid; trifluoromethanesulfonic acid; p-toluenesulfonic acid;

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N-methylacetamide; N-methylpropionamide; benzamide; diphenylphosphine; dimethyl malonate; diethyl malonate; dimethyl methylmalonate; diethyl methylmalonate; diethyl ethylmalonate; methyl acetoacetate; ethyl acetoacetate; ethyl

- 5 2-ethylacetoacetate; 1,3-pentanedione; dibenzoylmethane; methyl phenylacetate; methyl isobutyrate; acetophenone; tert-butyl methyl ketone and phenylacetone.

- The molar ratio of reagent M^1-Y-R^3 to the metallocene halide, in particular the metallocene dichloride (e.g. of the formula III) is generally in the range from 5 : 1 to 0.8 : 1, preferably from 2.5 : 1 to 0.9 : 1.

- The concentration of metallocene dichloride (e.g. of the formula 15 IIa) or of reagent M^1-Y-R^3 in the reaction mixture is generally in the range from 0.001 mol/l to 8 mol/l, preferably from 0.01 to 3 mol/l, particularly preferably from 0.05 mol/l to 2 mol/l.

- The reaction time for the reaction of the metallocene dichloride 20 (e.g. of the formula IIa) with the reagent M^1-Y-R^3 is generally in the range from 5 minutes to 1 week, preferably from 15 minutes to 48 hours.

- After conversion of the metallocenes of the formulae (Ia) and 25 (IIa) into the metallocenes of the formulae (I) and (II), insoluble constituents such as the salts or metal oxyhalides formed are preferably separated off before the new metallocenes are crystallized. For this purpose, preference is given to filtering and extracting a solution or suspension of the new 30 metallocenes in the inert solvent or solvent mixture which has been used in the ligand exchange reaction. The recrystallization is preferably carried out in aprotic hydrocarbons, in particular polar aprotic hydrocarbons. Particular preference is given to toluene, hexane, heptane, xylene, tetrahydrofuran (THF), 35 dimethoxyethane (DME), toluene/THF, heptane/DME or toluene/DME.

- The solvent or solvent mixture used in the extraction is at a temperature in the range from 20°C to the boiling point of the solvent or solvent mixture. The extraction is preferably carried 40 out at 0-20°C below the boiling point.

The resulting solution of the new metallocene is possibly concentrated by evaporation and the new metallocene subsequently crystallizes out.

The crystallization is carried out at from -78°C to 200°C , preferably from -30°C to 110°C , particularly preferably from -15°C to 30°C .

- 5 The purified metallocene obtained by crystallization can in turn be isolated from the mother liquor by filtration techniques.

The process of the present invention enables at least twice as much metallocene to be purified in existing apparatuses as was possible hitherto. In preferred embodiments, this factor is substantially exceeded, so that costly capacity expansions can be avoided.

The metallocenes of the formulae I and II obtainable by the purification process of the present invention are highly active catalyst components for olefin polymerization. Depending on the substitution pattern of the ligands, the metallocenes can be obtained as an isomer mixture. For the polymerization, the metallocenes are preferably used as pure isomers.

- 20 Preference is given to using the pseudo-rac metallocenes of the formula II.

The metallocenes of the formulae I and II obtainable by the purification process of the present invention are particularly suitable as constituents of catalyst systems for preparing polyolefins by polymerization of at least one olefin in the presence of a catalyst comprising at least one cocatalyst and at least one metallocene. For the purposes of the present invention, the term polymerization encompasses both homopolymerization and copolymerization.

The metallocenes of the formulae I and II, in particular of the formula II, obtainable by the purification process of the present invention can be used for the polymerization of one or more olefins of the formula $\text{R}^{\alpha}\text{-CH=CH-R}^{\beta}$, where R^{α} and R^{β} are identical or different and are each a hydrogen atom or a hydrocarbon radical having from 1 to 20 carbon atoms, in particular from 1 to 10 carbon atoms, and R^{α} and R^{β} together with the atoms connecting them may form one or more rings. Examples of such olefins are 1-olefins having 2 - 40, preferably from 2 to 10, carbon atoms, e.g. ethene, propene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene or 1-octene, styrene, dienes such as 1,3-butadiene, 1,4-hexadiene, vinylnorbornene, norbornadiene, ethylnorbornadiene and cyclic olefins such as norbornene, tetracyclododecene or methylnorbornene. Preference is given to homopolymerizing ethylene or propylene or copolymerizing ethylene

with one or more cyclic olefins such as norbornene and/or one or more dienes having from 4 to 20 carbon atoms, e.g. 1,3-butadiene or 1,4-hexadiene. Examples of such copolymers are ethylene-norbornene copolymers, ethylene-propylene copolymers and
 5 ethylene-propylene-1,4-hexadiene copolymers.

The metallocenes of the formulae I and II obtained in the purification process of the present invention display olefin polymerization activities which are at least equal to and
 10 sometimes superior to those of the dihalide compounds, and the polyolefins obtained display a reduction in the proportion of undesirable low molecular weight extractables.

The polymerization is carried out at from - 60 to 300 °C ,
 15 preferably from 50 to 200 °C, very particularly preferably from 50 - 80 °C. The pressure is from 0.5 to 2000 bar, preferably from 5 to 64 bar.

The polymerization can be carried out in solution, in bulk, in
 20 suspension or in the gas phase, continuously or batchwise, in one or more stages. Preferred embodiments are gas-phase and bulk polymerization.

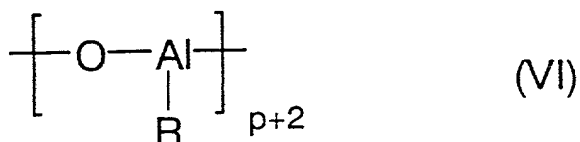
The catalyst used preferably comprises one of the metallocene
 25 compounds obtainable by the purification process of the present invention. It is also possible to use mixtures of two or more metallocene compounds, e.g. for preparing polyolefins having a broad or multimodal molar mass distribution.

30 The cocatalyst, which together with a metallocene of the formula I or II obtainable by the purification process of the present invention forms the catalyst system, comprises at least one compound such as an aluminoxane or a Lewis acid or an ionic compound which reacts with a metallocene to convert it into a
 35 cationic compound.

As aluminoxane, preference is given to using a compound of the formula (VII)

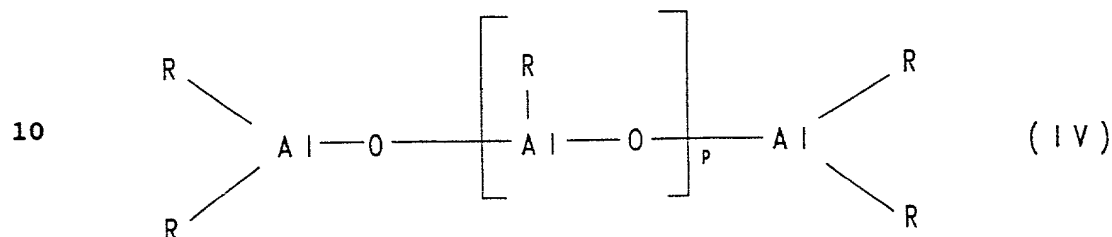
40 $(R AlO)_n$ (VII).

Further suitable aluminoxanes may be, for example, cyclic as in formula (VI)

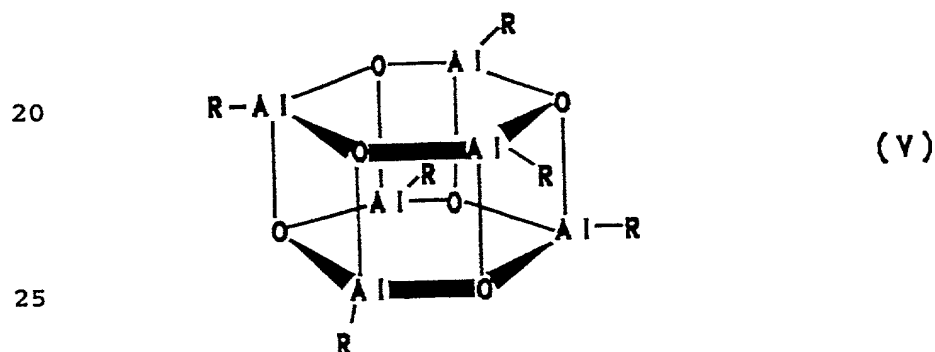


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or linear as in formula (IV)



15 or of the cluster type as in formula (V)



30 Such aluminoxanes are described, for example, in JACS 117 (1995), 6465-74, Organometallics 13 (1994), 2957-2969.

The radicals R in the formulae (IV), (V), (VI) and (VII) may be identical or different and may each be a C₁-C₂₀-hydrocarbon group
35 such as a C₁-C₆-alkyl group, a C₆-C₁₈-aryl group or benzyl, or hydrogen, and p is an integer from 2 to 50, preferably from 10 to 35.

The radicals R are preferably identical and are each methyl, 40 isobutyl, n-butyl, phenyl or benzyl, particularly preferably methyl.

If the radicals R are different, they are preferably methyl and hydrogen, methyl and isobutyl or methyl and n-butyl, with
45 hydrogen or isobutyl or n-butyl preferably being present in an amount of 0.01 - 40% (number of radicals R).

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The aluminoxane can be prepared in various ways by known methods. One of the methods is, for example, reacting an aluminum-hydrocarbon compound and/or a hydridoaluminum-hydrocarbon compound with water (gaseous, solid, liquid or bound - for example as water of crystallization) in an inert solvent (e.g. toluene).

To prepare an aluminoxane having different alkyl groups R, two different trialkylaluminums ($\text{AlR}_3 + \text{AlR}'_3$) corresponding to the desired composition and reactivity are reacted with water (cf. S. Pasynkiewicz, Polyhedron 9 (1990) 429 and EP-A-0,302,424).

Regardless of the method of preparation, all aluminoxane solutions have a variable content of unreacted aluminum starting compound which is present in free form or as adduct.

As Lewis acid, preference is given to using at least one organoboron or organoaluminum compound containing $\text{C}_1\text{-C}_{20}$ groups such as branched or unbranched alkyl or haloalkyl, e.g. methyl, propyl, isopropyl, isobutyl, trifluoromethyl, unsaturated groups such as aryl or haloaryl, e.g. phenyl, tolyl, benzyl, p-fluorophenyl, 3,5-difluorophenyl, pentachlorophenyl, pentafluorophenyl, 3,4,5-trifluorophenyl and 3,5-di(trifluoromethyl)phenyl.

Examples of Lewis acids are trimethylaluminum, triethylaluminum, triisobutylaluminum, tributylaluminum, trifluoroborane, triphenylborane, tris(4-fluorophenyl)borane, tris(3,5-difluorophenyl)borane, tris(4-fluoromethylphenyl)borane, tris(pentafluorophenyl)borane, tris(tolyl)borane, tris(3,5-dimethylphenyl)borane, tris(3,5-difluorophenyl)borane, $[(\text{C}_6\text{F}_5)_2\text{BO}]_2\text{Al-Me}$, $[(\text{C}_6\text{F}_5)_2\text{BO}]_3\text{Al}$ and/or tris(3,4,5-trifluorophenyl)borane. Particular preference is given to tris(pentafluorophenyl)borane.

As ionic cocatalysts, preference is given to using compounds containing a noncoordinating anion, for example tetrakis(pentafluorophenyl)borates, tetraphenylborates, SbF_6^- , CF_3SO_3^- or ClO_4^- . As cationic counterion, use is made of protonated Lewis bases such as methylamine, aniline, dimethylamine, diethylamine, N-methylaniline, diphenylamine, N,N-dimethylaniline, trimethylamine, triethylamine, tri-n-butylamine, methyldiphenylamine, pyridine, p-bromo-N,N-dimethylaniline, p-nitro-N,N-dimethylaniline, triethylphosphine, triphenylphosphine, diphenylphosphine, tetrahydrothiophene or triphenylcarbenium.

Examples of such ionic compounds are

- triethylammonium tetra(phenyl)borate,
- tributylammonium tetra(phenyl)borate,
- 5 trimethylammonium tetra(tolyl)borate,
- tributylammonium tetra(tolyl)borate,
- tributylammonium tetra(pentafluorophenyl)borate,
- tributylammonium tetra(pentafluorophenyl)aluminate,
- tripropylammonium tetra(dimethylphenyl)borate,
- 10 tributylammonium tetra(trifluoromethylphenyl)borate,
- tributylammonium tetra(4-fluorophenyl)borate,
- N,N-dimethylanilinium tetra(phenyl)borate,
- N,N-diethylanilinium tetra(phenyl)borate,
- N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate,
- 15 N,N-dimethylanilinium tetrakis(pentafluorophenyl)aluminate,
- di(propyl)ammonium tetrakis(pentafluorophenyl)borate,
- di(cyclohexyl)ammonium tetrakis(pentafluorophenyl)borate,
- triphenylphosphonium tetrakis(phenyl)borate,
- triethylphosphonium tetrakis(phenyl)borate,
- 20 diphenylphosphonium tetrakis(phenyl)borate,
- tri(methylphenyl)phosphonium tetrakis(phenyl)borate,
- tri(dimethylphenyl)phosphonium tetrakis(phenyl)borate,
- triphenylcarbenium tetrakis(pentafluorophenyl)borate,
- triphenylcarbenium tetrakis(pentafluorophenyl)aluminate,
- 25 triphenylcarbenium tetrakis(phenyl)aluminate,
- ferrocenium tetrakis(pentafluorophenyl)borate and/or
- ferrocenium tetrakis(pentafluorophenyl)aluminate.
- Preference is given to triphenylcarbenium
- tetrakis(pentafluorophenyl)borate and/or
- 30 N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate.

It is also possible to use mixtures of at least one Lewis acid and at least one ionic compound.

- 35 Further suitable cocatalyst components are borane or carborane compounds such as
- 7,8-dicarbaundecaborane(13),
- undecahydrido-7,8-dimethyl-7,8-dicarbaundecaborane,
- 40 dodecahydrido-1-phenyl-1,3-dicarbanonaborane,
- tri(butyl)ammonium undecahydrido-8-ethyl-7,9-dicarbaundecaborate,
- 4-carbanonaborane(14),
- bis(tri(butyl)ammonium) nonaborate,
- bis(tri(butyl)ammonium) undecaborate,
- 45 bis(tri(butyl)ammonium) dodecaborate,
- bis(tri(butyl)ammonium) decachlorodecaborate,
- tri(butyl)ammonium 1-carbadecaborate,

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- tri(butyl)ammonium 1-carbadodecaborate,
 tri(butyl)ammonium 1-trimethylsilyl-1-carbadecaborate,
 tri(butyl)ammonium
 bis(nonahydrido-1,3-dicarbanonaborato)cobaltate(III),
 5 tri(butyl)ammonium
 bis(undecahydrido-7,8-dicarbaundecaborato)ferrate(III).

- Further cocatalysts which can be used in unsupported or supported form are the compounds specified in EP-A-0924223, DE-A-19622207,
 10 EP-A-0601830, EP-A-0824112, EP-A-0824113, WO 99/06414, EP-A-0811627 and DE-A-19804970.

- The support component of the catalyst system of the present invention may be any organic or inorganic, inert solid, in
 15 particular a porous support such as talc, inorganic oxides and finely divided polymer powders (e.g. polyolefins).

- Suitable inorganic oxides may be found among the oxides of elements of groups 2,3,4,5,13,14,15 and 16 of the Periodic Table
 20 of the Elements. Examples of oxides preferred as supports include silicon dioxide, aluminum oxide and also mixed oxides of the two elements and corresponding oxide mixtures. Other inorganic oxides which can be used alone or in combination with the abovementioned preferred oxidic supports are, for example, MgO, ZrO₂, TiO₂ or
 25 B₂O₃, to name only a few.

- The support materials used have a specific surface area in the range from 10 to 1000 m²/g, a pore volume in the range from 0.1 to 5 ml/g and a mean particle size of from 1 to 500 µm. Preference
 30 is given to supports having a specific surface area in the range from 50 to 500 m²/g, a pore volume in the range from 0.5 to 3.5 ml/g and a mean particle size in the range from 5 to 350 µm. Particular preference is given to supports having a specific surface area in the range from 200 to 400 m²/g, a pore volume in
 35 the range from 0.8 to 3.0 ml/g and a mean particle size of from 10 to 200 µm.

- If the support material used naturally has a low moisture content or residual solvent content, dehydration or drying before use can
 40 be omitted. If this is not the case, for example when using silica gel as support material, dehydration or drying is advisable. Thermal dehydration or drying of the support material can be carried out under reduced pressure with simultaneous inert gas blanketing (e.g. nitrogen). The drying temperature is in the
 45 range from 100 to 1000 °C, preferably from 200 to 800 °C. The parameter pressure is not critical in this case. The duration of the drying process can be from 1 to 24 hours. Shorter or longer

drying times are possible, provided that equilibrium with the hydroxyl groups on the support surface can be established under the conditions chosen, which normally takes from 4 to 8 hours.

- 5 Dehydration or drying of the support material can also be carried out by chemical means, by reacting the adsorbed water and the hydroxyl groups on the surface with suitable passivating agents. Reaction with the passivating reagent enables all or some of the hydroxyl groups to be converted into a form which leads to no
- 10 adverse interaction with the catalytically active centers. Suitable passivating agents are, for example, silicon halides and silanes, e.g. silicon tetrachloride, chlorotrimethylsilane, dimethylaminotrichlorosilane, or organometallic compounds of aluminum, boron and magnesium, for example trimethylaluminum,
- 15 triethylaluminum, triisobutylaluminum, triethylborane, dibutylmagnesium. Chemical dehydration or passivation of the support material is carried out, for example, by reacting a suspension of the support material in a suitable solvent with the passivating reagent in pure form or as a solution in a suitable
- 20 solvent in the absence of air and moisture. Suitable solvents are, for example, aliphatic or aromatic hydrocarbons such as pentane, hexane, heptane, toluene or xylene. Passivation is carried out at from 25 °C to 120 °C, preferably from 50 to 70 °C. Higher and lower temperatures are possible. The reaction time is
- 25 from 30 minutes to 20 hours, preferably from 1 to 5 hours. After chemical dehydration is complete, the support material is isolated by filtration under inert conditions, washed one or more times with suitable inert solvents as have been described above and subsequently dried in a stream of inert gas or under reduced
- 30 pressure.

- Organic support materials such as finely divided polyolefin powders (e.g. polyethylene, polypropylene or polystyrene) can also be used and should likewise be freed of adhering moisture,
- 35 solvent residues or other impurities by means of appropriate purification and drying operations before use.

- The catalyst system is prepared by mixing at least one metallocene as rac-meso isomer mixture, at least one cocatalyst
- 40 and at least one passivated support.

- To prepare the supported catalyst system, at least one of the above-described metallocene components obtainable by the purification process of the present invention is brought into
- 45 contact with at least one cocatalyst component in a suitable solvent, preferably giving a soluble reaction product, an adduct or a mixture.

30

The composition obtained in this way is then mixed with the dehydrated or passivated support material, the solvent is removed and the resulting supported metallocene catalyst system is dried to ensure that all or most of the solvent is removed from the
5 pores of the support material. The supported catalyst is obtained as a free-flowing powder.

A process for preparing a free-flowing and possibly prepolymerized supported catalyst system comprises the following
10 steps:

- a) preparing a metallocene/cocatalyst mixture in a suitable solvent or suspension medium, where the metallocene component is obtainable from the purification process of the present
15 invention and has one of the above-described structures;
 - b) applying the metallocene/cocatalyst mixture to a porous, preferably inorganic dehydrated support;
 - c) removing the major part of the solvent from the resulting mixture;
 - 20 d) isolating the supported catalyst system;
 - e) if desired, prepolymerizing the supported catalyst system obtained using one or more olefinic monomer(s) to give a prepolymerized supported catalyst system.
- 25 Preferred solvents for preparing the metallocene/cocatalyst mixture are hydrocarbons and hydrocarbon mixtures which are liquid at the chosen reaction temperature and in which the individual components preferably dissolve. However, solubility of the individual components is not a prerequisite as long as it is
30 ensured that the reaction product of metallocene and cocatalyst components is soluble in the solvent selected. Examples of suitable solvents include alkanes such as pentane, isopentane, hexane, heptane, octane and nonane; cycloalkanes such as cyclopentane and cyclohexane; and aromatics such as benzene,
35 toluene, ethylbenzene and diethylbenzene. Very particular preference is given to toluene.

The amounts of aluminoxane and metallocene used in the preparation of the supported catalyst system can be varied over a
40 wide range. Preference is given to a molar ratio of aluminum to transition metal in the metallocene of from 10 : 1 to 1000 : 1, very particularly preferably from 50 : 1 to 500 : 1.

In the case of methylaluminoxane, preference is given to using
45 30% strength toluene solutions; however, the use of 10% strength solutions is also possible.

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For preactivation, the solid metallocene is dissolved in a solution of the aluminoxane in a suitable solvent. It is also possible to dissolve the metallocene separately in a suitable solvent and subsequently to combine this solution with the
 5 aluminoxane solution. Preference is given to using toluene.

The preactivation time is from 1 minute to 200 hours.

The preactivation can take place at room temperature (25 °C). The
 10 use of higher temperatures can in some cases shorten the preactivation time required and result in an additional increase in the activity. In this case, higher temperature means a range from 50 to 100 °C.

15 The preactivated solution or metallocene/cocatalyst mixture is subsequently combined with an inert support material, usually silica gel, in the form of a dry powder or as a suspension in one of the abovementioned solvents. The support material is preferably used as a powder. The order of addition is immaterial.

20 The preactivated metallocene/cocatalyst solution or metallocene/cocatalyst mixture can be added to the support material or the support material can be introduced into the solution.

25 The volume of the preactivated solution or metallocene/cocatalyst mixture can exceed 100% of the total pore volume of the support material used or else can be up to 100% of the total pore volume.

The temperature at which the preactivated solution or
 30 metallocene/cocatalyst mixture is brought into contact with the support material can vary in the range from 0 to 100 °C. However, lower or higher temperatures are also possible.

Subsequently, all or most of the solvent is removed from the
 35 supported catalyst system, with the mixture being able to be stirred and also heated if desired. Preference is given to removing both the visible proportion of the solvent and also the proportion in the pores of the support material. The removal of the solvent can be carried out in a conventional way using
 40 reduced pressure and/or flushing with inert gas. In the drying process, the mixture can be heated until the free solvent has been removed, which usually takes from 1 to 3 hours at a preferred temperature of from 30 to 60 °C. The free solvent is the visible proportion of solvent in the mixture. For the purposes of
 45 the present invention, residual solvent is the proportion enclosed in the pores.

As an alternative to complete removal of the solvent, the

supported catalyst system can also be dried only to a certain residual solvent content, with the free solvent having been completely removed. The supported catalyst system can subsequently be washed with a low-boiling hydrocarbon such as pentane or hexane and dried again.

After it has been prepared, the supported catalyst system can either be used directly for the polymerization of olefins or be prepolymerized using one or more olefinic monomers prior to use in a polymerization process. The prepolymerization of supported catalyst systems is described, for example, in WO 94/28034.

As additive, a small amount of an olefin, preferably a α -olefin (for example styrene or phenyldimethylvinylsilane) as activity-promoting component, or, for example, an antistatic can be added during or after the preparation of the supported catalyst system.

As antistatic, use is customarily made of a mixture of a metal salt of Medialan acid, a metal salt of anthranilic acid and a polyamine. Such antistatics are described, for example, in EP-A-0,636,636.

The molar ratio of additive to metallocene component (compound (I)) is preferably from 1 : 1000 to 1000 : 1, very particularly preferably from 1 : 20 to 20 : 1.

The present invention also provides a process for preparing a polyolefin by polymerization of one or more olefins in the presence of the catalyst system comprising at least one transition metal component of the formula I or II which is obtainable by the purification process of the present invention. For the purposes of the present invention, the term polymerization encompasses both homopolymerization and copolymerization.

The metallocenes of the formulae I and II obtained in the purification process of the present invention display olefin polymerization activities which are at least equal to and sometimes superior to those of the dihalide compounds, and the polyolefins obtained display a reduction in the proportion of undesirable low molecular weight extractables.

The catalyst system described here can be used as sole catalyst component for the polymerization of olefins having from 2 to 20 carbon atoms, but is preferably used in combination with at least one alkyl compound of elements of main group I to III of the

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Periodic Table, e.g. an aluminum alkyl, magnesium alkyl or lithium alkyl or an aluminoxane. The alkyl compound is added to the monomers or the suspension medium and serves to free the monomers of substances which can adversely affect the catalyst activity. The amount of alkyl compound added depends on the quality of the monomers used.

As molar mass regulator and/or to increase the activity, hydrogen is added if required.

10

In the polymerization, the antistatic can be introduced into the polymerization system either together with or separately from the catalyst system used.

- 15 The polymers prepared using the catalyst system comprising at least one of the metallocenes of the formulae I and II obtained in the purification process of the present invention display a uniform particle morphology and contain no fines. No deposits or caked material occur in the polymerization using the catalyst system.
- 20

The catalyst system gives polymers such as polypropylene with extraordinarily high stereospecificity and regiospecificity.

- 25 The stereospecificity and regiospecificity of polymers, particularly polypropylene, is defined, in particular, by the triad tacticity (TT) and the proportion of 2-1-inserted propene units (RI), which can be determined from the ^{13}C -NMR spectra.

- 30 The ^{13}C -NMR spectra are measured in a mixture of hexachlorobutadiene and d_2 -tetrachloroethane at elevated temperature (365 K). All ^{13}C -NMR spectra of the polypropylene samples measured are calibrated on the basis of the resonance signal of d_2 -tetrachloroethane ($\delta = 73.81 \text{ ppm}$).

35

To determine the triad tacticity of the polypropylene, the methyl resonance signals in the ^{13}C -NMR spectrum from 23 to 16 ppm are examined; cf. J. C. Randall, Polymer Sequence Determination: Carbon-13 NMR Method, Academic Press New York 1978; A. Zambelli,

- 40 P. Locatelli, G. Bajo, F. A. Bovey, Macromolecules 8 (1975), 687-689; H. N. Cheng, J. A. Ewen, Makromol. Chem. 190 (1989), 1931-1943. Three successive 1-2-inserted propene units whose methyl groups are on the same side in the "Fischer projection" are referred to as mm triads ($\delta = 21.0 \text{ ppm}$ to 22.0 ppm). If only the second methyl group of three successive propene units points to the other side, one speaks of an rr triad ($\delta = 19.5 \text{ ppm}$ to 20.3 ppm) and if only the third methyl group of the three successive

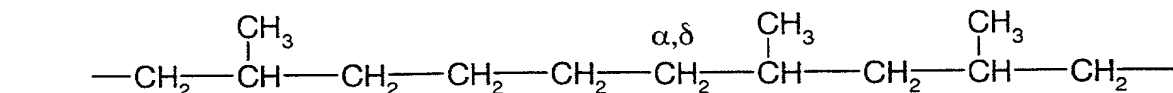
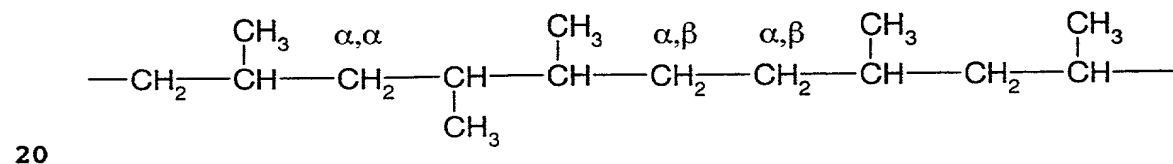
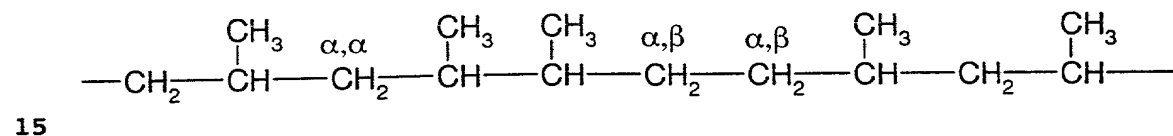
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propene units points to the other side, this is referred to as an mr triad ($\delta = 20.3$ ppm to 21.0 ppm). The triad tacticity is calculated according to the following formula:

$$5 \quad TT (\%) = mm / (mm + mr + rr) \cdot 100$$

If a propene unit is inserted inversely into the growing polymer chain, this is referred to as a 2-1 insertion; cf. T. Tsutsui, N. Ishimaru, A. Mizuno, A. Toyota, N. Kashiwa, Polymer 30, (1989),

10 1350-56. The following structural arrangements are possible:



25 The proportion of 2-1-inserted propene units (RI) can be calculated according to the following formula:

$$RI (\%) = 0.5 I_{\alpha, \beta} (I_{\alpha, \alpha} + I_{\alpha, \beta} + I_{\alpha, \delta}) \cdot 100,$$

30 where

$I_{\alpha, \alpha}$ is the sum of the intensities of the resonance signals at $\delta = 41.84, 42.92$ and 46.22 ppm,

35 $I_{\alpha, \beta}$ is the sum of the intensities of the resonance signals at $\delta = 30.13, 32.12, 35.11$ and 35.57 ppm

and

40 $I_{\alpha, \delta}$ is the intensity of the resonance signal at $\delta = 37.08$ ppm.

The isotactic polypropylene which has been prepared using the catalyst system has a proportion of 2-1-inserted propene units RI of $< 0.5\%$ at a triad tacticity TT of $> 98.0\%$ and a melting point 45 of $> 153^\circ\text{C}$, and the M_w/M_n of the polypropylene prepared according to the present invention is from 2.5 to 3.5.

35

The copolymers which can be prepared using the catalyst system have a significantly higher molar mass than those of the prior art. At the same time, the use of the catalyst system enables such copolymers to be prepared with high productivity at 5 industrially relevant process parameters without deposit formation.

The polymers prepared by the process are particularly useful for producing hard and stiff shaped bodies having a high tensile 10 strength, for example fibers, filaments, injection-molded parts, films, sheets or large hollow bodies (e.g. pipes).

The invention is illustrated by the following nonlimiting examples.

15

General procedures: preparation and handling of organometallic compounds was carried out in the absence of air and moisture under argon (Schlenk technique or glove box). All solvents required were purged with argon and dried over molecular sieves 20 before use.

Example 1: Dimethylsilanediylbis(2-methyl-4,5-benzoindenyl)zirconium monochloride mono(2,4-di-tert-butylphenoxide) (1)

25

20.6 g (0.1 mol) of 2,4-di-tert-butylphenol in 200 ml of toluene/20 ml of THF were admixed at room temperature with 37.2 ml (0.1 mol) of a 20% strength solution of butyllithium in toluene. The mixture was stirred for another 1 hour at 60°C. At 30 room temperature, 28.8 g (0.05 mol) of dimethylsilanediyl-bis(2-methyl-4,5-benzoindenyl)zirconium dichloride were added as a solid. The suspension was stirred at 100°C for 3 hours and subsequently filtered hot through Celite. The filter cake was extracted 3 times with 100 ml each time of 35 toluene (100°C). After evaporation of the solvent, the yellow solid which had precipitated was filtered off and dried under reduced pressure. This gave 31.1 g (83%) of dimethylsilanediylbis(2-methyl-4,5-benzoindenyl)zirconium monochloride mono(2,4-di-tert-butylphenoxide) (1).

40

¹H-NMR (400 MHz, CDCl₃): 8.05 (dd, 1H), 7.75 (m, 2H), 7.65 (dd, 1H), 7.60 (1H), 7.5 - 7.15 (m, 6H), 7.1 (m, 1H), 7.0 (m, 1H), 6.85 (s, 1H), 6.8 (d, 1H), 6.65 (m, 1H), 5.45 (d, 1H), 2.82 (s, 3H), 2.45 (s, 3H), 1.45 (s, 3H), 1.35 (s, 3H), 1.25 (s, 9H), 45 0.95 (s, 9H).

Solubility comparison:

50 mg of
dimethylsilanediylbis(2-methyl-4,5-benzoindenyl)zirconium
5 dichloride dissolved completely in 240 ml of toluene at room
temperature (solubility: about 0.36 mmol/l).

50 mg of the compound (1) dissolved immediately in < 5 ml of
toluene at room temperature (solubility: > 13 mmol/l).

10

Example 1a: Preparation of a catalyst using (1) and
polymerization:

35.1 mg (0.047 mmol) of (1) were stirred in 2.1 ml of 30%
15 strength MAO solution in toluene (Al/Zr=215) for 60 minutes at
room temperature. 2 g of SiO₂ (Grace XPO2107, pretreated at 140°C,
10 mbar, 10 hours) were subsequently added and the mixture was
stirred for another 10 minutes. The solvent was removed in an oil
pump vacuum.

20

A dry 2 l reactor was flushed firstly with nitrogen and
subsequently with propylene and charged with 1.5 l of liquid
propylene. 2 ml of TEA (20% strength in Varsol) were added
thereto and the mixture was stirred for 15 minutes. The catalyst
25 system prepared above (0.886 g) was subsequently resuspended in
20 ml of heptane and then injected into the reactor and rinsed in
with 15 ml of heptane. The reaction mixture was heated to the
polymerization temperature of 60°C and polymerization was carried
out for 1 hour. The polymerization was stopped by venting the
30 remaining propylene. The polymer was dried in a vacuum drying
oven. This gave 470 g of polypropylene powder. The reactor
displayed no deposits on the inner wall or stirrer. The catalyst
activity was 0.53 kg of PP/g of catalyst x h.

35 Comparative example:

Preparation of a catalyst using
dimethylsilanediylbis(2-methyl-4,5-benzoindenyl)zirconium
dichloride and polymerization

40

27.1 mg (0.047 mmol) of
dimethylsilanediylbis(2-methyl-4,5-benzoindenyl)zirconium
dichloride were stirred in 2.1 ml of 30% strength MAO solution in
toluene (Al/Zr=215) for 60 minutes at room temperature. 2 g of
45 SiO₂ (Grace XPO2107, pretreated at 140°C, 10 mbar, 10 hours) were

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subsequently added and the mixture was stirred for another 10 minutes. The solvent was removed in an oil pump vacuum.

- A dry 2 l reactor was flushed firstly with nitrogen and
- 5 subsequently with propylene and charged with 1.5 l of liquid propylene. 2 ml of TEA (20% strength in Varsol) were added thereto and the mixture was stirred for 15 minutes. The catalyst system prepared above (0.897 g) was subsequently resuspended in 20 ml of heptane and then injected into the reactor and rinsed in
 - 10 with 15 ml of heptane. The reaction mixture was heated to the polymerization temperature of 60°C and polymerization was carried out for 1 hour. The polymerization was stopped by venting the remaining propylene. The polymer was dried in a vacuum drying oven. This gave 410 g of polypropylene powder. The reactor
 - 15 displayed no deposits on the inner wall or stirrer. The catalyst activity was 0.46 kg of PP/g of catalyst x h.

Example 2: Dimethylsilanediyl-bis(2-methylindenyl)zirconium monochloride mono(2,4-di-tert-butylphenoxide) (2)

- 20 1.03 g (5 mmol) of 2,4-di-tert-butylphenol in 10 ml of toluene/1 ml of THF were admixed at room temperature with 1.85 ml (5 mmol) of a 20% strength solution of butyllithium in toluene. The mixture was stirred for another 1 hour at 60°C. At room
- 25 temperature, 1.19 g (2.5 mmol) of dimethylsilanediyl-bis(2-methylindenyl)zirconium dichloride were added as a solid. The suspension was stirred at 60°C for 2 hours and subsequently filtered hot through Celite. The filter cake was extracted 3 times with 10 ml each time of toluene (60°C). After
- 30 evaporation of the solvent, the yellow solid which had precipitated was filtered off and dried under reduced pressure. This gave 0.87 g (53%) of dimethylsilanediylbis(2-methylindenyl)zirconium monochloride mono(2,4-di-tert-butylphenoxide) (2).
- 35 ¹H-NMR (400 MHz, CDCl₃): 8.03 (dd, 1H), 7.6 (dd, 1H), 7.25 - 7.2 (m, 2H), 7.15 (m, 1H), 7.1-7.0 (m, 2H), 6.9 (m, 1H), 6.8 (s, 1H), 6.75 (m, 1H), 6.7 (m, 1H), 6.3 (s, 1H), 5.55 (d, 1H), 2.65 (s, 3H), 2.3 (s, 3H), 1.3 (s, 3H), 1.25 (s, 9H), 1.22 (s, 3H), 1.15
- 40 (s, 9H).

Solubility comparison:

- 50 mg of dimethylsilanediylbis(2-methylindenyl)zirconium
- 45 dichloride dissolved completely in 50 ml of toluene at room temperature (solubility: about 2.1 mmol/l).

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50 mg of the compound (2) dissolved immediately in < 5 ml of toluene at room temperature (solubility: > 15 mmol/l).

Example 3: Dimethylsilanediylbis(2-methyl-4,5-benzoindenyl)zirconium monochloride mono(2-isopropyl-5-methylphenoxide) (3)

2.7 g (17.4 mmol) of 2-isopropyl-5-methylphenol in 20 ml of toluene/2 ml of THF were admixed at room temperature with 6.5 ml (17.4 mmol) of a 20% strength solution of butyllithium in toluene. The mixture was stirred for another 1 hour at 60°C. At room temperature, 5.0 g (8.7 mmol) of dimethylsilanediylbis(2-methyl-4,5-benzoindenyl)zirconium dichloride were added as a solid. The suspension was stirred at 100°C for 4 hours and subsequently filtered hot through Celite. The filter cake was extracted twice with 25 ml each time of toluene (100°C). After evaporation of the solvent, the yellow solid which had precipitated was filtered off and dried under reduced pressure. This gave 2.5 g (41%) of dimethylsilanediylbis(2-methyl-4,5-benzoindenyl)zirconium monochloride mono(2-isopropyl-5-methylphenoxide) (3).

¹H-NMR (400 MHz, CDCl₃): 7.9 (dd, 1H), 7.81 (m, 1H), 7.74 (m, 1H), 7.54 (m, 2H), 7.45 - 7.08 (m, 8H), 6.65 (d, 1H), 6.55 (s, 1H), 6.35 (m, 1H), 5.56 (d, 1H), 2.58 (s, 3H), 2.35 (s, 3H), 2.3 (m, 1H), 2.1 (s, 3H), 1.37 (s, 3H), 1.27 (s, 3H), 0.75 (d, 3H), 0.62 (d, 3H).

Solubility comparison:

50 mg of dimethylsilanediylbis(2-methyl-4,5-benzoindenyl)zirconium dichloride dissolved completely in 240 ml of toluene at room temperature (solubility: about 0.36 mmol/l).

50 mg of the compound (3) dissolved in 4 ml of toluene at room temperature (solubility: about 18 mmol/l).

Example 4: Dimethylsilanediylbis(2-methylindenyl)zirconium monochloride mono(2-isopropyl-5-methylphenoxide) (4)

3.2 g (21 mmol) of 2-isopropyl-5-methylphenol in 20 ml of toluene/2 ml of THF were admixed at room temperature with 7.8 ml (21 mmol) of a 20% strength solution of butyllithium in toluene. The mixture was stirred for another 1 hour at 60°C. At room temperature, 5.0 g (10.5 mmol) of dimethylsilanediylbis(2-methylindenyl)zirconium dichloride were

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added as a solid. The suspension was stirred at 100°C for 2 hours and subsequently filtered hot through Celite. The filter cake was extracted twice with 25 ml each time of toluene (100°C). After evaporation of the solvent, the yellow solid which had

5 precipitated was filtered off and dried under reduced pressure.

This gave 1.36 g (22%) of

dimethylsilanediylbis(2-methylindenyl)zirconium monochloride mono(2-isopropyl-5-methylphenoxide) (4).

10 ¹H-NMR (400 MHz, CDCl₃): 8.0 (m, 1H), 7.81 (m, 1H), 7.3 - 6.8 (m, 8H), 6.55 (dm, 1H), 6.1 (s, 1H), 5.9 (d, 1H), 2.7 (hept, 1H), 2.45 (s, 3H), 2.25 (s, 3H), 2.18 (s, 3H), 1.4 (s, 3H), 1.25 (s, 3H), 1.1 (d, 3H), 0.95 (d, 3H).

15 Solubility comparison:

50 mg of dimethylsilanediylbis(2-methylindenyl)zirconium dichloride dissolved completely in 50 ml of toluene at room temperature (solubility: about 2.1 mmol/l).

20

50 mg of the compound (4) dissolved in 5 ml of toluene at room temperature (solubility: about 17 mmol/l).

Example 5: Dimethylsilanediylbis(2-methylindenyl)zirconium monochloride mono(2,4-dimethylphenoxide) (5)

25

1.0 g (8.2 mmol) of 2,4-dimethylphenol in 20 ml of toluene/2 ml of THF were admixed at room temperature with 3.0 ml (8.2 mmol) of a 20% strength solution of butyllithium in toluene. The mixture
30 was stirred for another 1 hour at 60°C. At room temperature, 1.9 g (4.0 mmol) of dimethylsilanediylbis(2-methylindenyl)zirconium dichloride were added as a solid. The suspension was stirred at 60°C for 8 hours and subsequently filtered hot through Celite. After evaporation of the solvent to about 7 ml, the yellow solid
35 which had precipitated at -30°C was filtered off and dried under reduced pressure. This gave 0.65 g (29%) of dimethylsilanediylbis(2-methylindenyl)zirconium monochloride mono(2,4-dimethylphenoxide) (5).

40 ¹H-NMR (400 MHz, CDCl₃): 7.96 (dd, 1H), 7.6 (m, 1H), 7.36 (m, 1H), 7.31 (m, 1H), 7.29 (d, 1H), 7.1 (m, 1H), 6.99 (m, 1H), 6.94 (m, 1H), 6.88 (s, 1H), 6.75 (m, 1H), 6.65 (m, 1H), 6.06 (s, 1H), 5.93 (d, 1H), 2.4 (s, 3H), 2.24 (s, 3H), 2.18 (s, 3H), 1.85 (s, 3H), 1.35 (s, 3H), 1.24 (s, 3H).

45

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Example 6: Dimethylsilanediylbis(2-methyl-4,5-benzoindenyl)-
zirconium monochloride mono(2,4-di-tert-
pentylphenoxide) (6)

- 5 0.85 g (3.5 mmol) of 2,4-di-tert-pentylphenol in 10 ml of
toluene/1 ml of THF were admixed at room temperature with 1.3 ml
(3.5 mmol) of a 20% strength solution of butyllithium in toluene.
The mixture was stirred for another 1 hour at 60°C. At room
temperature, 1.0 g (1.74 mmol) of dimethylsilanediylbis(2-methyl-
10 4,5-benzoindenyl)zirconium dichloride were added as a solid. The
suspension was stirred at 100°C for 4 hours, diluted with 40 ml of
toluene and subsequently filtered hot through Celite. The filter
cake was extracted twice with 25 ml each time of toluene (100°C).
After evaporation of the solvent to 10 ml, the yellow solid which
15 had precipitated was filtered off, washed with a little cold
toluene and dried under reduced pressure. This gave 0.85 g (63%)
of dimethylsilanediylbis(2-methyl-4,5-benzoindenyl)zirconium
monochloride mono(2,4-di-tert-pentylphenoxide) (6).
- 20 ¹H-NMR (400 MHz, CDCl₃): 8.00 (d, 1H), 7.74 (t, 2H), 7.64-7.57 (m,
2H), 7.45 - 7.27 (m, 5H), 7.14 (s, 1H), 7.10 (m, 1H), 6.98 (m,
1H), 6.78 (s, 1H), 6.65 (d, 1H), 6.52 (dd, 1H), 5.38 (d, 1H),
2.78 (s, 3H), 2.41 (s, 3H), 1.46 (quart., 2H), 1.41 (s, 3H),
1.30 (s, 3H), 1.22 (m, 2H), 1.14 (s, 3H), 1.13 (s, 3H), 0.91 (s,
25 3H), 0.88 (s, 3H), 0.57 (t, 3H), 0.39 (t, 3H).

Solubility comparison:

- 50 mg of dimethylsilanediylbis(2-methyl-
30 4,5-benzoindenyl)zirconium dichloride dissolved completely in
240 ml of toluene at room temperature (solubility: about
0.36 mmol/l).

- 55 mg of the compound (6) dissolved in 4 ml of toluene at room
35 temperature (solubility: about 17.7 mmol/l).

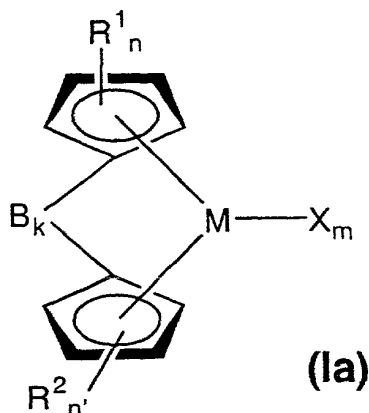
We claim:

1. A process for purifying compounds of the formula (Ia)

5

10

15



where

- 20 M is a metal of transition group III, IV, V or VI of the Periodic Table of the Elements, in particular Ti, Zr or Hf, particularly preferably zirconium,
- 25 R^1 are identical or different and are each a radical SiR_3^{12} , where R^{12} are identical or different and are each a hydrogen atom or a C_1 - C_{40} group, preferably C_1 - C_{20} -alkyl, C_1 - C_{10} -fluoroalkyl, C_1 - C_{10} -alkoxy, C_6 - C_{20} -aryl, C_6 - C_{10} -fluoroaryl, C_6 - C_{10} -aryloxy, C_2 - C_{10} -alkenyl, C_7 - C_{40} -arylalkyl, C_7 - C_{40} -alkylaryl or C_8 - C_{40} -arylalkenyl,
- 30 or R^1 is a C_1 - C_{30} group, preferably C_1 - C_{25} -alkyl such as methyl, ethyl, tert-butyl, cyclohexyl or octyl, C_2 - C_{25} -alkenyl, C_3 - C_{15} -alkylalkenyl, C_6 - C_{24} -aryl, C_5 - C_{24} -heteroaryl, C_7 - C_{30} -arylalkyl, C_7 - C_{30} -alkylaryl, fluorinated C_1 - C_{25} -alkyl, fluorinated C_6 - C_{24} -aryl, fluorinated
- 35 C_7 - C_{30} -arylalkyl, fluorinated C_7 - C_{30} -alkylaryl or C_1 - C_{12} -alkoxy, or two or more radicals R^1 may be joined to one another in such a way that the radicals R^1 and the atoms of the cyclopentadienyl ring which connect them form a C_4 - C_{24} -ring
- 40 system which may in turn be substituted,
- R^2 are identical or different and are each a radical SiR_3^{12} , where R^{12} are identical or different and are each a hydrogen atom or a C_1 - C_{40} group, preferably C_1 - C_{20} -alkyl,
- 45 C_1 - C_{10} -fluoroalkyl, C_1 - C_{10} -alkoxy, C_6 - C_{14} -aryl, C_6 - C_{10} -fluoroaryl, C_6 - C_{10} -aryloxy, C_2 - C_{10} -alkenyl, C_7 - C_{40} -arylalkyl, C_7 - C_{40} -alkylaryl or C_8 - C_{40} -arylalkenyl,

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- or R^2 is a C_1 - C_{30} group, preferably C_1 - C_{25} -alkyl such as methyl, ethyl, tert-butyl, cyclohexyl or octyl, C_2 - C_{25} -alkenyl, C_3 - C_{15} -alkylalkenyl, C_6 - C_{24} -aryl, C_5 - C_{24} -heteroaryl, C_7 - C_{30} -arylalkyl, C_7 - C_{30} -alkylaryl, fluorinated C_1 - C_{25} -alkyl, fluorinated C_6 - C_{24} -aryl, fluorinated C_7 - C_{30} -arylalkyl, fluorinated C_7 - C_{30} -alkylaryl or C_1 - C_{12} -alkoxy,
- or two or more radicals R^2 may be joined to one another in such a way that the radicals R^2 and the atoms of the cyclopentadienyl ring which connect them form a C_4 - C_{24} ring system which may in turn be substituted,
- X is a halogen atom, in particular chlorine,
- n is from 1 to 5 when $k = 0$, and n is from 0 to 4 when $k = 1$,
- 15 n' is from 1 to 5 when $k = 0$, and n' is from 0 to 4 when $k = 1$,
- m is from 1 to 4, preferably 2,
- k is zero or 1, where the metallocene is unbridged when $k = 0$ and is bridged when $k = 1$, with preference being given to $k = 1$, and
- 20 B is a bridging structural element between the two cyclopentadienyl rings,

comprising the steps:

- 25 a) reacting the compound of the formula (Ia) with a ligand exchange component



- 30 where

- M^1 is a cation or a cationic fragment, in particular Li, Na, K, MgCl, MgBr, MgI, or is an ammonium cation corresponding to an amine,
- 35 R^3 is hydrogen or a C_1 - C_{40} group, preferably C_1 - C_{25} -alkyl such as methyl, ethyl, tert-butyl, cyclohexyl or octyl, C_2 - C_{25} -alkenyl, C_3 - C_{15} -alkylalkenyl, C_6 - C_{24} -aryl, C_5 - C_{24} -heteroaryl such as pyridyl, furyl or quinolyl, C_7 - C_{30} -arylalkyl, C_7 - C_{30} -alkylaryl, fluorinated C_1 - C_{25} -alkyl, fluorinated C_6 - C_{24} -aryl, fluorinated C_7 - C_{30} -arylalkyl or fluorinated C_7 - C_{30} -alkylaryl,
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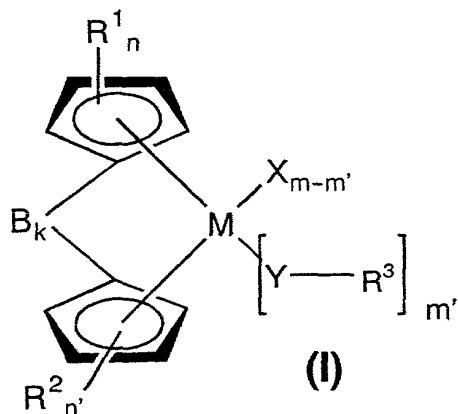
Y is an element of main group 6 of the Periodic Table of the Elements, in particular oxygen or sulfur, or a fragment CR^3_2 , NR^3 , $\text{NR}^3(\text{CO})-$, $\text{NR}^3(\text{SO}_2)-$, PR^3 or $\text{P}(=\text{O})\text{R}^3$, $\text{O}(\text{CO})-$, $\text{O}(\text{SO}_2)-$,

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to form the compound of the formula (I)

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where

M, R^1 , R^2 , R^3 , X, Y, n, n', m, k, B and R^{12} are as defined above and

m' is from 1 to 4, preferably 1 or 2,

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with the compound of the formula M^1X , where M^1 and X are as defined above, being eliminated, in an inert solvent or solvent mixture,

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- b) if desired, separating off solid residues of the formula M^1X
- c) if desired, separating off the inert solvent or solvent mixture,
- d) recrystallizing the compound of the formula (I) from an aprotic hydrocarbon,
- e) separating the compound of the formula (I) from the mother liquor.

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2. A process as claimed in claim 1, wherein a polar or nonpolar, aprotic hydrocarbon or hydrocarbon mixture is used in step d).

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3. A process as claimed in claim 1 or 2, wherein toluene, hexane, heptane, xylene, tetrahydrofuran (THF), dimethoxyethane (DME), toluene/THF, heptane/DME or toluene/DME is used in step d).

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4. The use of a compound obtained as set forth in claim 1 for preparing a catalyst system for the polymerization of olefins.

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5. A catalyst system comprising at least one compound obtained as set forth in claim 1 and a support and, if desired, a cocatalyst.
6. A process for preparing a polyolefin in the presence of a catalyst system as claimed in claim 5.
7. The use of a catalyst as claimed in claim 5 for the polymerization of one or more olefins.

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Purification of metallocenes

Abstract

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A process for purifying metallocenes in which a sparingly soluble metallocene halide is converted into a readily soluble and readily crystallizable metallocene by replacement of at least one halide ligand by an alternative negatively charged ligand and the
10 metallocene obtained in this way is subsequently purified by crystallization.

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Declaration, Power of Attorney

Page 1 of 3

0732/990001

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Purification of metallocenes

the specification of which

☒ is attached hereto.

☐ was filed on _____ as

Application Serial No. _____

and amended on _____.

☒ was filed as PCT international application

Number PCT/EP99/08849

on November 18, 1999

and was amended under PCT Article 19

on _____ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
19900585.0	Germany	11 January 1999	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
19854350.6	Germany	25 November 1998	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.

Filing Date

Status (pending, patented,
abandoned)

_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

And we (I) hereby appoint **Messrs. HERBERT B. KEIL**, Registration Number 18,967; and **RUSSEL E. WEINKAUF**, Registration Number 18,495; the address of both being Messrs. Keil & Weinkauff, 1101 Connecticut Ave., N.W., Washington, D.C. 20036 (telephone 202-659-0100), our attorneys, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to sign the drawings, to receive the patent, and to transact all business in the Patent Office connected therewith.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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